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O. F. Williams

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INTRODUCTION

Clay, because of its widespread occurrence and utilization, is one of the most common of naturally occurring substances. In spite of the familiarity of the term "clay", its precise definition is not easy to formulate. The Committee on Sedimentation of the National Research Council and the American Ceramic Society, based on independent studies of present and past usage of the term, have published definitions which have been found satisfactory (1,2). The term "clay", as used today carries with it three implications; (a) a natural material with plastic properties, (b) an essential composition of particles of very fine size grades, and (c) an essential composition of crystalline fragments of minerals that are essentially hydrous aluminum silicates or occasionally hydrous magnesium silicates (3).

Clays are formed as the result of physical disintegration and chemical weathering of igneous, metamorphic, and sedimentary rocks. According to method of formation, clays may be classified as being either residual or sedimentary depending upon whether the clay is found associated with its parent rock or whether it has been transported from its origin to a new environment. Sedimentary clays are more homogeneous in physical and mineral characteristics than residual clays. Because of their homogeneity, sedimentary clays are most widely used for the manufacture of structural products (4).

In industrial terminology, there are over fifty different classifications of clay according to use. Among the most familiar of these are ball clays, china clays, fire clays, brick clays, Fuller's earth, etc. (1).

As the result of certain fundamental studies in the last twenty years, classification of clays according to composition and structure has been made possible. With respect to composition and structure, the term "clay material" is preferred as a general term rather than clay. Extensive research has established beyond doubt that clay materials have as their major constituents crystalline particles of minerals known as the "clay minerals". The clay minerals are hydrous aluminum silicates in which replacement of aluminum by iron and magnesium occurs frequently in addition to the presence of small amounts of the alkalies and alkaline earths. The principal clay minerals are kaolinite, montmorillonite and illite. Almost all clays are composed of one or more of these fundamental minerals plus others which are of lesser importance and which generally occur only in minor amounts such as halloysite, attapulgite, allophane and chloritic mica. The present knowledge of clay mineral composition and structure has come to be known as the "clay mineral concept" (5).

CHEMICAL AND PHYSICAL CHARACTERISTICS

The clay mineral concept of the structure and composition of clay materials has provided the basis for recent fundamental studies of clays with respect to their properties. Experimental methods employed in the study of the physical characteristics of clays involve interpretation of data obtained by means of the microscope, X-rays, electron microscope, and differential thermal analysis. Microscopic examination of clay materials reveals that

the clay minerals occur in extremely small, flat, flake-shaped particles which are probably monoclinic. Information obtained from electron microscope studies indicates that clay minerals can exist in particles approaching their unit cell height (about 0.001mm.) (6)(7). Application of X-ray diffraction to lattice structure studies of the clay minerals in the last twenty years along with Pauling's generalizations has resulted in fairly well established structures of the more important clay minerals (8)(6). In general two structural units are involved in the atomic lattices of clay minerals. One unit, known as the alumina or aluminum hydroxide unit, consists of two sheets of closely packed oxygen or hydroxyls between which aluminum atoms are embedded in such a position that they are equidistant from oxygens or hydroxyls. This is essentially a gibbsite structure in as much as only two-thirds of the possible aluminum positions are occupied in this unit. The second fundamental unit consists of a sheet of tetrahedral silica groups linked to form a hexagonal network. The generally accepted montmorillonite structure consists of structural units of one gibbsite sheet between two sheets of tetrahedral silica groups. The structural units are stacked one above another and are loosely held together with water present between the units. The unit cell dimension perpendicular to the planes of the silica tetrahedral layers varies with water content; the mineral is said to have an expanding lattice. At least part of the magnesium ions usually found associated with montmorillonite are thought to exist as replacements of aluminum positions in the gibbsite layer thereby providing an excess charge on the lattice. The charge so produced is assumed to have the strength necessary to hold exchangeable bases but is not sufficiently strong to hold together tightly the units making up montmorillonite. Furthermore, hydration of exchangeable cations would be expected to have an additional effect of pushing the units further apart. As a consequence of these hydration effects, the units of the montmorillonite are very readily cleaved, by such mild treatment as agitation in water, into extremely thin flakes giving a huge surface area to a mass of the mineral. A rather unusual property of the montmorillonite lattice is that aluminum can be removed by acid leaching until the ratio of Al to Si atoms is 1.7 to 4 before the lattice structure is destroyed (9).

The lattice structure of illite is similar to that of montmorillonite except that about 15 per cent of the silicon positions are replaced by aluminum and the resulting excess charges are neutralized by potassium ions between the silica sheets of two successive units. Like montmorillonite, illite has a pronounced basal cleavage but to a lesser extent than the former. Illite unit layers do not expand and are held together to the extent that the mineral does not tend to break down by agitation in water into as small, or as thin flakes as montmorillonite (10).

The kaolinite structure is composed of a gibbsite sheet along with a single sheet of tetrahedral silica groups. Water has no expansion effect on the lattice; no replacements of the aluminum by iron or magnesium in the gibbsite lattice have been observed (11).

Differential thermal analysis provides another approach to the experimental investigation of the structure of clay. Differential thermal analysis detects and indicates the thermal effects that accompany the loss of water, decomposition or changes in crystal structure that occur when a clay is heated. Essentially the procedure is one which a sample being analyzed is set adjacent to a sample of a thermally inert material (usually alumina) and both are heated at a fairly rapid and same constant rate of temperature rise. A differential thermocouple is used to measure the difference

in temperature between the two samples and simultaneously a regular thermocouple measures the rate of temperature rise. Any changes in the clay sample, such as loss of water or lattice changes, are indicated by the differential temperature readings. Changes which take place during the heating period appear as peaks on the thermal analysis curve obtained by plotting differential temperature readings against temperature (12)(13). Differential thermal analysis applied to montmorillonite yields a thermal analysis curve with three endothermic peaks, one at 250°C representing loss of water held between basal planes of the lattice structure, a second peak between 600°C and 700°C corresponding to the loss of lattice water and a third peak at 900°C corresponding to the final breakdown of the lattice. The illite thermal analysis curve shows three initial endothermic peaks corresponding to the changes described for montmorillonite and in addition an exothermic peak immediately following the third endothermic peak. The exothermic peak is thought to be associated with the formation of spinel. A kaolinite thermal analysis curve reveals one endothermic peak representing the dehydration of the mineral and an exothermic peak which is attributed to the formation of $-Al_2O_3$ (14)(15).

Chemical characteristics of clay are for the most part related to the "base-exchange capacity" of its clay mineral constituents. The property of clay materials to carry exchangeable cations is designated as "base-exchange capacity". Exchangeable cations involved in base exchange may be either organic or inorganic. The character and degree of base-exchange capacity is determined to a large extent upon two competing factors maintaining electrical neutrality of a particular lattice unit of clay mineral. Substitution of silicon by aluminum in the lattice leaves the lattice negatively charged. This is balanced by a second factor which is compensation of charge by cations external to a layer, the exchangeable ones (16). The relative ease of replacement of one cation for another depends on the relative size, charge and degree of hydration of the cations involved. The following series representing the relative ease of replacement of one cation by another has been widely accepted: $Li > Na > \dots > K > Rb > Cs > Mg > Ca > Sr > Ba > H >$ (17). Organic cations can participate in base-exchange reactions as indicated by the color reactions of primary aromatic amines with kaolinite and montmorillonite. All shades of the spectrum may be produced by treating these clay minerals with different types of aromatic amines (18)(19)(20).

Application of information obtained from fundamental studies of clay materials have been widespread and are becoming even more so. In ceramic engineering, clays of the kaolinite type are most widely used because of their properties of plasticity and low drying shrinkage both of which are closely connected with the kaolinite lattice structure which as previously mentioned is of the non-expanding type. Clays play an important role in chemical research and development as catalysts for organic reactions and as absorbents of color from oils and solvents. A recent statement published in "Chemical and Engineering News" (21) points out that every kind of organic reaction has been shown to be catalyzed by one or another of the available types of clay. Clay is an important constituent of soil inasmuch as its base-exchange properties make cations necessary for plant growth easily accessible. The type of clay mineral present also determines to a large extent the quantity of moisture a particular soil may retain (22). In construction engineering the civil engineer must in most cases rely on the soil to carry the load of a given structure and here again the physical and chemical characteristics of the clay materials present must be known (23).

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Organic Derivatives of Lead

G. L. Eichhorn

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The organic derivatives of Group IV elements reveal striking analogies all the way from carbon to lead, with decreasing similarities as the differences in atomic size of the elements become greater. The lead compounds are unique in some respects; in others they resemble markedly their tin analogs. Although the stable oxidation state of lead is +2 in inorganic compounds, most organic lead compounds are tetravalent (1).

I. Alkyl and Aryl Lead Compounds

A. Preparation

The original synthesis of tetraethyl lead (from ethyl iodide and lead-sodium alloy), now markedly improved, is still the basis for its commercial preparation (1). Other routes leading to the formation of tetra-alkyl and tetra-aryl derivatives are the reactions of lead with alkyl iodide, and of lead chloride with alkyl or aryl zinc, Grignard reagent (1), or lithium aryls (1935). The last two reagents can be used for the production of compounds having two different organic radicals attached to the lead nucleus, if organic lead halides are substituted for lead chloride. (13, 20, 21, 24, 54).

(Many of these reactions are equally applicable to the tin analogs (67, 71). Formation of what has been believed to be a carbon-tin double bond has not been duplicated with the lead compounds (63).

B. Properties

The lead tetra-alkyls are colorless liquids, with a specific gravity greater than that of water. Their boiling points rise with increasing molecular weight and increasing molecular symmetry, the latter effect being the more important. The specific gravity decreases with increasing molecular weight and increases with increasing symmetry. (1, 20).

The tetra-aryls are crystallible white solids, stable at their melting points, insoluble in water, but quite soluble in benzene, carbon disulfide, and chloroform (1).

An optically active compound containing an asymmetric lead atom has been prepared, but could not be resolved (6).

C. Reactions

Thermal decomposition of tetra-alkyl lead (42, 46, 51) leads to the formation of free radicals. Alkalies and dilute acids have no effect, but strong or concentrated acids (as well as silver and copper nitrates) will substitute acid radicals for one or two of the organic groups (1, 26, 34). When two or more radicals are involved, aryls, light alkyls, and heavy aryls are cleaved in preference to alkyls, heavy alkyls, and light aryls, respectively, (1, 3, 25, 26). The more labile groups may be replaced by means of lithium alkyl (21).

These compounds are not generally oxidized by potassium permanganate (4); they can be decomposed by nickel and hydrogen into metallic lead and dialkyl or diaryl (2). Aluminum chloride brings about a partial interchange of halogen with organic groups (18).

II. Organic Lead Halides

A. Trisubstituted Lead Halides (R_3PbX)

Compounds of this type may be prepared from tetra-alkyl or -aryl lead by controlled reactions with halogen, halogen acid or mercuric halide (22); by Grignard from lead chloride (41); and from dialkyl lead dihalide with lead-sodium alloys. (Most of these methods are also applicable to the organic tin halides.)

The trialkyl lead halides are soluble in water, liquid ammonia, and organic solvents. In aqueous solution they dissociate into X^- and R_3Pb^+ . The latter ion resembles in many respects the alkali metal cations. The lead-carbon linkage in these compounds is covalent, whereas the lead-halogen linkage is electrovalent. The solubility decreases as the atomic weight of the halogen increases (1).

With sodium hydroxide or silver oxide, potassium cyanide, and sodium sulfide, trialkyl lead halide can be converted to the hydroxide, cyanide, and sulfide, respectively (12). The reaction with magnesium yields tetra-alkyl lead and a Grignard reagent.

B. Disubstituted Lead Dihalides (R_2PbX_2)

The dihalides can be prepared from tetra-substituted lead by treatment with halogen acid (22), mercuric chloride (45) or sodium halide (50); also indirectly, through the diacetates, from dialkyl mercury and lead tetra-acetate. The heavier halides can be converted to the fluorides with potassium fluoride (49). (The corresponding tin compounds can be prepared directly from tin and alkyl iodide, and from dialkyl mercury and stannous halide.)

The dihalides are less stable than the monohalides, sometimes decomposing into lead halide and dialkyl or diaryl. The R_2Pb^{+2} ion resembles Zn^{+2} ion. The solubility of dialkyl lead dichloride increases with molecular weight (1).

C. $RPbX_3$

Only one reaction, that between $CsPbX_3$ and the alkyl iodide, has been found to yield alkyl lead trihalides. These compounds are converted to the trihydroxides by aqueous ammonia (37). (The corresponding tin compounds can be synthesized from $KSnX_3$ (59).)

III. Oxygen Compounds

A. Plumbols (R_3PbOH)

The carbinol analogs are prepared by alkaline hydrolysis of the trisubstituted lead halides (11). Their basic strength is of the order of sodium hydroxide. Reactions include the precipitation of the heavy metals, displacement of ammonia from ammonium salts, and the formation of insoluble sulfides with hydrogen sulfide (1).

Substances in which the plumbolichydroxyl group has been replaced by a phenolic group (15) are synthesized from tetra-alkyl lead and the corresponding phenol. Esters of the type $R_3PbOCOR$ (23) are formed from tetra-alkyl lead and an organic acid. They are crystalline solids with low water solubility.

3. Plumbones and Plumbonic Acids

The ketone analogs of lead can be made by oxidation of the plumbols (45) with mercuric oxide, or hydrolysis of R_2Pb^{+2} salts (49).

The treatment of an alkyl halide with $NaPb(OH)_3$ (36, 39), or hydrolysis of alkyl lead trichloride (38) results in the formation of a compound $RPb(OH)_3$ or $RPbOOH$. These substances are rather unstable, especially in a moist atmosphere. Their salts are soluble in alkali, but insoluble in aqueous ammonia. The action of halogen acid reconverts them to the trihalides; when heated in a sealed tube, decomposition into lead oxide, alcohol, and water takes place.

IV. Diplumbanes and Di- and Tri- Valent Lead

A. R_3Pb

Compounds having the empirical formula R_3Pb result from the Grignard reaction between lead chloride and $RMgX$ (1), reduction of plumbols (28), electrolytic reduction of acetone at a lead electrode (17), reaction of lead chloride with lithium alkyl or aryl (5), and the Fittig synthesis with trisubstituted lead halides (19). The alkyls are greenish-yellow liquids, whose stability increases with the length of the alkyl groups; the aryls are readily crystallizable greenish-yellow solids (1, 14).

Magnetic susceptibility measurements indicate that PbR_3 monomer does not exist in appreciable quantity (43, 48); cryoscopic examination, however, points to some dissociation of Pb_2R_6 (33). Electron diffraction experiments indicate a tetrahedral configuration for this compound (52).

Tri-o-tolyl lead is converted to tetra-o-tolyl lead in xylene solution. Hydrogen bromide yields the tri-o-tolyl bromide (2). Thermal decomposition of a mixture of hexamethyl- and hexaethyl- diplumbane results in the formation of all possible lead tetra-alkyls (30). Iodine, sodium, and maleic anhydride add to tri-alkyl and triaryl lead (19, 29). As with tetrasubstituted lead, an exchange of radicals can be brought about by treatment with lithium alkyl (21).

B. Divalent lead (R_2Pb)

Disubstituted lead (PbR_2) can be prepared from lead chloride and lithium alkyl or aryl, or Grignard reagents, under special conditions (1, 5). (These preparations resemble those of diphenyl tin (55, 56).) Diphenyl lead is a blood-red, amorphous solid, very soluble in benzene, less soluble in ether, and insoluble in water (1). It reacts with iodine to give diphenyl. (Diphenyl tin and bromine yield stable, diphenyl tin dibromide (55). Pyrolysis of diphenyl tin produces hexaphenyl distamane and metallic tin.)

(C. Higher Tin Homologs)

In the pyrolysis of diphenyl tin, dodecaphenyl pentastannane is isolated among other products (57). A series of reactions starting with dimethyl tin dibromide can be effected to synthesize dodecamethyl pentastannane, as well as symmetrical diethylhexamethyl stannopropane (63).

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V. Coordination Compounds.

Divalent lead salts form interesting compounds with tartaric (47) and salicylic acids (53, 56), as well as hydroxy quinone (40), dimethyl glyoxime (32), and other substances, in all of which two positions are available for bonding with a lead atom.

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Ward B. Schaap

October 6, 1948

I. URANIUM COMPOUNDS

A. BINARY COMPOUNDS WITH ELEMENTS (Non-Solvent Chemistry)

1. HYDROGEN^{1,2,3} reacts with massive uranium metal to yield a hydride, UH_3 , in the form of a very fine, highly pyrophoric gray powder with a density (X-ray) of 10.9 and possessing a simple cubic lattice. In pure hydrogen the reaction begins immediately at 325° , which is the temperature of maximum reaction rate¹. This compound is unique in that it is not typical of any of the three classes of hydrides. It resembles the salt-like hydrides most closely, since it has a definite composition, a high melting point, is brittle and possesses a structure unrelated to that of uranium metal, being almost lacking in metal to metal bonds. Rundle² proposed U-H-U bridges between metal atoms, where each bridge contains one pair of electrons for two bonds. Deuterium reacts similarly², yielding a deuteride having lattice spacings definitely smaller than those of the usual hydride.

2. BORON reportedly forms the boride UB_4 , obtainable by electrolysis of a mixture of a borate and a fluoride of uranium⁴, or by thermal decomposition of uranous borohydride^{2,3}.

3. CARBON and uranium form three carbides, two of which were first reported by Manhattan Project workers.

UC (Monocarbide)⁵ can be separated from U metal of low carbon content by dissolving the metal in acid. It has face-centered cubic structure, probably of NaCl type.

U_2C_3 (Sesquicarbide)⁵ exists only at temperatures greater than 2000° .

UC_2 (Dicarbide)⁵ was previously known and described. It is similar to CaC_2 in structure, though quite different chemically. X-ray and chemical studies show that carbon is soluble in UC_2 , and if quenched that the resulting cell has smaller dimensions than before. This decrease may be explained either by (a) a uranium atom being occasionally replaced by a carbon atom or C_2 group, or (b) the structure containing excess carbon must be thought of as a UC_2 lattice deficient in uranium, thus allowing the cell dimensions to shrink slightly.

4. NITROGEN. UN (Mononitride)⁵ is the lowest nitride. It has a face centered cubic lattice probably of the NaCl type. Both uranium and nitrogen are negligibly soluble in UN.

U_2N_3 (Sesquinitride)⁵ has a body-centered cubic structure and is isomorphous with manganese sesquinitride.⁵

UN_2 (Dinitride)(and intermediate phase)⁵. When U_2N_3 is treated with excess nitrogen a one-phase gradual and continuous transition occurs until the composition UN_2 is reached. Only the two limiting compositions, U_2N_3 and UN_2 , are regarded as true compounds. At a nitrogen pressure of one atmosphere, the composition is about $\text{UN}_{1.75}$, which accounts for references to odd formulas, such as U_4N_7 , in older literature. This solubility of nitrogen in U_2N_3 is due to the fact that the sesquinitride conforms to a distorted fluorite (CaF_2) type structure with nitrogen atoms missing in a regular way from the lattice. As nitrogen is added the distortion decreases until with the composition UN_2 the ideal fluorite structure is attained. The crystal structure does not change throughout this transition.

5. OXYGEN and uranium form a series of compounds similar to the carbides and nitrides.

UO (Monoxide)⁵ has a face-centered cubic, NaCl type structure. It has been prepared only in minute amounts and is known

solely from X-ray data. UO was initially observed when X-ray diffraction studies were made on uranium metal at higher temperatures. A surface film on the metal caused a cubic structure to be observed rather than that of the metal. The principle light element in this film was found to be oxygen.

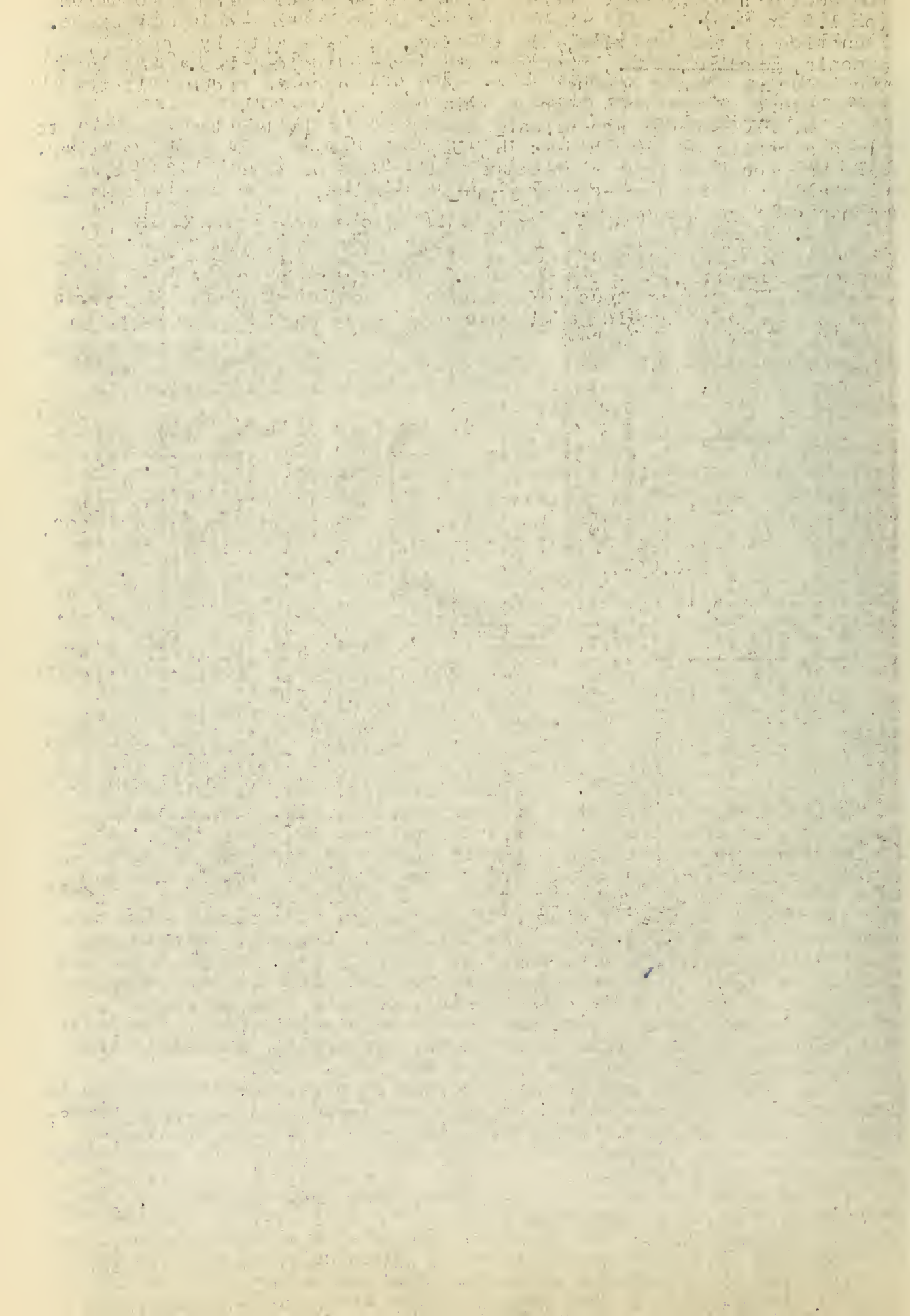
UO₂ (Dioxide)⁵ has been long known. Its ideal lattice constant is $a = 5.4531\text{\AA}$, but a wide variation in spacing is possible. Thus, when heated with excess uranium, the spacing increases to 5.4610\AA as the uranium atoms fill vacant interstices in the dioxide structure. Heating with excess oxygen decreases the lattice constant to 5.4397\AA , but causes no change in structure until the oxygen content goes beyond UO_{2.25}, at which point a discontinuity occurs. UO₂ has the fluorite-type lattice and this may be considered a simple cubic lattice of oxygen ions with U⁴⁺ ions in half of the cubic interstices. If the oxygen ion lattice remains fixed and the U⁴⁺ ions are occasionally missing at random, then the lattice would be allowed to shrink slightly. The decrease in spacing with increasing oxygen content is difficult to understand if the additional oxygen is interstitial. Hence it is felt that the solubility is due to absence of tetravalent uranium ions.

Higher Oxides^{5,6,7} occur in the form of U₂O₅, U₃O₈, several forms of UO₃ and as hydrated UO₄. The oxides UO₃, U₃O₈, and U₂O₅ all have similar structures since a one-phase region extends from the composition UO₃ down to UO_{2.25}, and the basic structure over this entire range is orthorhombic. Thus, when UO₂ is heated with oxygen its fluorite structure is maintained until the composition UO_{2.25} is reached. Above this point of discontinuity orthorhombic U₂O₅ appears, and a single orthorhombic phase then persists until the composition UO₃ is reached. Jolibois⁸ reported the existence of U₃O₇, a compound having X-ray diffraction patterns very similar to those of UO₂ and different from those of U₃O₈. If true, this would indicate that the UO₂-type single phase region may extend to UO_{2.33}.

All of the oxides, with the exceptions of UO and U₂O₅⁹, are easily obtained¹⁰. The olive green to black uranous oxide, U₃O₈, is obtained when the other oxides are heated in air at about 800°. Its composition is not strictly constant but varies with the temperature of ignition, the oxygen content decreasing with increasing temperature over 800°. Uranium trioxide, UO₃, is obtained as an orange powder by ignition of the peroxide, UO₄, the ammonium diuranate, or uranyl nitrate at a temperature of about 300°. At higher temperatures reduction occurs unless atmospheres of pure oxygen or H₂O₄ are employed. The yellow peroxide, UO₄¹⁰, has not been obtained in the anhydrous state. The dihydrate exists at 100°, but decomposes to UO₃ at higher temperatures. Its formula can be represented as H₂O.UO₃.H₂O₂ or as UO₄.2H₂O. UO₄.nH₂O is pptd. by the addition of hydrogen peroxide to slightly acid uranyl solutions (pH 1.5 to 2.5)¹¹. It can be coprecipitated with thorium peroxide. Reduction of the peroxide, the dioxide, or U₃O₈ with hydrogen¹⁰, ammonia, alcohol, etc., produces the brown dioxide, UO₂. The last two reducing agents produce a reactive, pyrophoric product if the temperature of the reduction is kept low, e.g. 350°.

6. PHOSPHOROUS and uranium combine at elevated temperatures to yield a series of phosphides: UP, UP₂ and U₃P₄¹², all gray in color. U₃P₄ was found to have a structure like that of Th₃P₄, while UP crystallizes in a face-centered cubic lattice, as do the mononitride monocarbide and monoxide.

7. SULFUR forms the sulfides US₂, US₃, U₂S₃ and U₄S₃¹³. The disulfide, US₂, is prepared by high temperature reaction of H₂S on uranous compounds, e.g. the dioxide. It is also precipitated as hydrated US₂ from uranous solutions by ammonium sulfide. US₃ has been prepared by heating a mixture of US₂ and sulfur in a sealed tube¹³. U₂S₃ and U₄S₃ have been prepared from pure U filings and sulfur, and their formation established by X-ray methods¹³. US₂.



is reduced by hydrogen to U_2S_3 , but not to a monosulfide¹⁵.

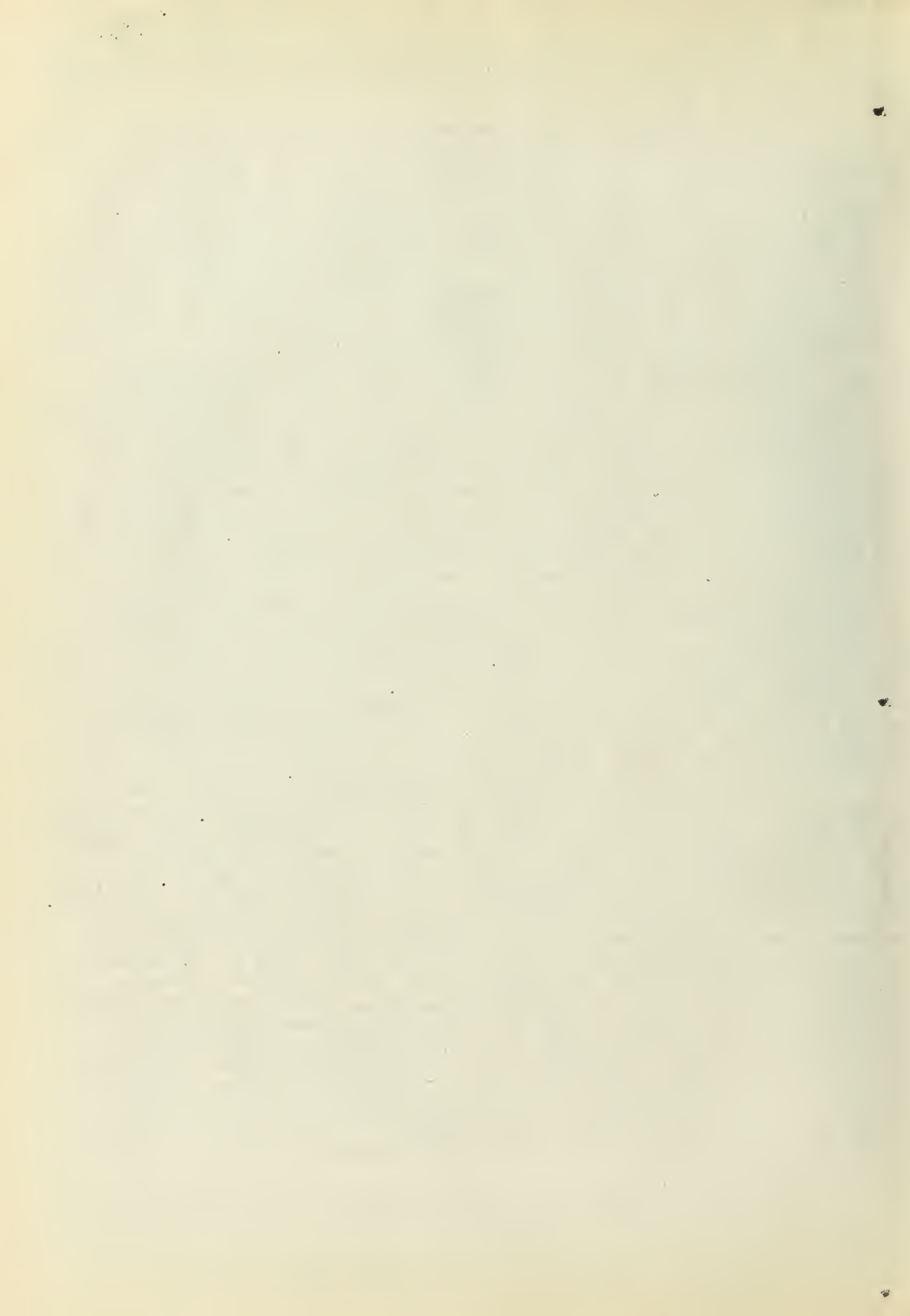
8. THE HALOGENS form with uranium the compounds types UX_3 , UX_4 , UX_5 , UX_6 , UOX_2 and UO_2X_2 . The oxyhalides are highly ionic compounds, while the ionic character of the binary halides decreases with increasing charge on the uranium atom, UX_3 and UX_4 being much more ionic than UX_5 .

The trivalent uranium compounds with Cl, Br, and I are readily prepared by the action of the corresponding anhydrous hydrogen halide gas on uranium hydride at moderate temperatures, e.g. 250-300°. Hydrogen fluoride forms only UF_3 under these conditions. Treatment of the tetravalent halides, UCl_4 , UBr_4 or UI_4 with H_2 produces the UX_3 compounds. These salts are highly ionic, very soluble in water giving a red solution of trivalent uranium ions. The solution is not stable, for the U^{+3} ions react with the water liberating hydrogen and forming a green solution of tetravalent uranium. The solid halide compounds range in color from green-brown to brown and may be stored in dry air.

Tetravalent uranium compounds with all the halogens are known, and these are the most stable of the binary-type halogen compounds (Only UO_2X_2 compounds are more stable). With the exception of the fluoride, the tetravalent halides are very soluble in water imparting to the solution the deep green color characteristic of uranous ($+4$) ions. The fluoride is insoluble in water and may be precipitated as $UF_4 \cdot 2H_2O$ from strong sulfuric acid solutions. These compounds are prepared in the anhydrous state by the action of halogen gases, X_2 , on uranium metal or the hydride. Treatment of UO_2 or other uranous salts with anhydrous hydrogen halide gases also yields UX_4 . Special preparative reactions¹⁶ used are chlorinations with carbon tetrachloride of UO_2 , U_3O_8 , UO_3 , UO_2Cl_2 or $U(C_2O_4)_2$ at about 400-500° to give principally UCl_4 and small amounts of $COCl_2$, Cl_2 and UCl_5 . The higher oxides give more UCl_5 by-product than does the dioxide. Small amounts of carbon are mixed with the higher oxides to increase UCl_4 yield. Other chlorinating agents, e.g. S_2Cl_2 , $SOCl_2$ and even $MoCl_5$ ¹⁷ have been used. Freon and UO_3 react to give UF_4 of high purity¹⁷. The tetrafluoride exists as a non-hygroscopic, dense, bright green powder, while the others are olive green to brownish and are very hygroscopic.

Only two binary halides of pentavalent and hexavalent uranium are known; they are the fluorides and chlorides. Consideration of size relationships indicate that the hexaiodide and possibly the hexabromide cannot exist. If, then, as suggested by some^{18a}, the pentahalides are actually double salts of the type $UX_4 \cdot UX_6$, the non-existence of the pentabromide and pentaiodide are explained. Further evidence in favor of the double formula lies in the observed ease of disproportionation of UCl_5 into UCl_4 and UCl_6 and in the fact that molecular weight studies show UCl_5 to be dimeric in carbon tetrachloride solution, having the empirical formula U_2Cl_{10} , which can also be written $UCl_4 \cdot UCl_6$. Chlorination of the higher oxides of uranium with a mixture of carbon tetrachloride and chlorine, or treatment of UCl_4 with chlorine, produces the pentachloride, UCl_5 , as sublimate¹⁶. The pentachloride disproportionates in vacuo to UCl_4 and UCl_6 , with volatilization of the hexachloride above 150°. Liquid phase chlorinations of UO_3 or U_3O_8 with carbon tetrachloride at moderate temperatures and high pressures yield UCl_5 ^{19,19}. Very little mention is made of the pentafluoride, UF_5 ¹⁹.

Of the hexahalides, UF_6 has been known for many years¹⁸, while the hexachloride was reported only recently¹⁹. The hexafluoride is prepared by the action of fluorine gas on other uranium compounds at moderate temperatures---about 200-250°. It can be obtained in the form of pale yellow, monoclinic crystals^{18a} which sublime at



ordinary pressures, (b.p. is 53° and m.p. 69.5°) but can be melted at higher pressures. The solid and gas are extremely hygroscopic, hydrolyzing on contact with traces of water to the ionic salt uranyl fluoride, UO_2F_2 , and liberating HF. Thus UF_6 can be stored in glass without etching only if no water is present^{18b}. The solid hexafluoride is soluble in organic solvents; however, it reacts even in the cold with all but the most inert, forming UF_4 and fluorinating (in some cases charring) the solvent. The chlorinated hydrocarbons are good solvents^{18a}, but also react when warmed sufficiently, e.g. UF_6 and CCl_4 in a sealed tube react at temperatures above 70° to give UF_4 and freons. Freons are quite inert to the hexafluoride. The properties of the hexachloride, UOCl_6 , have not been described, but may be presumed to be similar to those of UF_6 , though perhaps it is less volatile¹⁸.

B. TERNARY AND MISCELLANEOUS URANIUM COMPOUNDS (Solution Chemistry)

1. TRIVALENT URANIUM. Only one solid compound has been obtained from a solution of trivalent uranium. It was prepared by adding conc. sulfuric acid to ice cold U (+3) solution. The crystals which appeared were assigned the formula $\text{U}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. Soluble salts cannot be crystallized by evaporation because of the reaction between trivalent uranium and water.

2. TETRAVALENT URANIUM forms two series of compounds; the greater number contain the U^{+4} ion while some apparently contain a UO^{++} group. In slightly acid uranous solutions most inorganic and organic acids form soluble uranous salts. Exceptions are the insoluble fluoride, the phosphates and ites, arsenates and ites, oxalate and iodate²⁹. In neutral or basic solution the soluble salts hydrolyze immediately precipitating the hydrated oxide, $\text{UO}_2 \cdot \text{H}_2\text{O}$ as a deep greenish-brown gelatinous ppt. the orthophosphates in acid solutions precipitate as a hydrated $\text{U}(\text{HPO}_4)_2$ or $\text{U}(\text{NH}_4\text{PO}_4)_2$ (if ammonium ions are present) in the form of greenish gelatinous precipitates which are insoluble in less than 1 N acid. Both of these ignite to the gray pyrophosphate, UP_2O_7 . The oxalate ppt. is also acid-insoluble, but it and UF_4 dissolve in presence of excess oxalate ions in neutral solution to form an oxalato complex.

Recently, Schlesinger and co-workers²³ prepared the borohydride of uranium (IV), $\text{U}(\text{BH}_4)_4$, and its alkyl derivatives. These compounds are by far the most volatile of uranous compounds, but are not very stable. The borohydride decomposes into the uranium (III) borohydride at $80-100^\circ$. At higher temperatures UB_4 is thought to be formed.

The oxy-compounds (UO^{++}) are not common. Some which have been reported are uranous oxyfluoride, $\text{UOF}_2 \cdot 2\text{H}_2\text{O}$ and the basic iodate, $\text{UO}(\text{IO}_3)_2$ ²¹. By reduction of uranyl pyrophosphate with hydrogen at high temperatures the uranous oxyphosphosphate, $(\text{UO})_2\text{P}_2\text{O}_7$, is obtained.

In general, the uranous resembles thorium in its chemistry²⁸. Its compounds, usually green in color, are essentially ionic but have some covalent character depending on the anion; e.g. the tetrachloride, UCl_4 can be volatilized at moderate temperatures and is soluble in organic solvents. There is a definite, but not strong tendency to complex.

3. PENTAVALENT URANIUM salts have not been prepared from solution. The two halides, UCl_5 and UF_5 , are obtained by "dry reactions" and are not stable in solution, disproportionating to give a solution containing uranous (IV) and uranyl ions. Initial evidence supporting the existence of pentavalent uranium at least temporarily in solution as "oxy" ions, UO_2^+ , has arisen through polarographic studies (see below). More recently, millimolar solutions of this pentavalent uranium ion were obtained by electrolysis of uranyl salts in perchlorate solution²⁴, but no compounds were reported.

4. HEXAVALENT URANIUM exists in two compound types, but only one of these is stable in aqueous solution. The stable type comprises the uranyl salts which contain the UO_2^{++} group. The two known salts of the other type, UF_6 and UCl_6 , hydrolyze to the uranyl salts upon contact with water. The uranyl salts are the most common and most important of the uranium compounds. They are, in general, yellow, fluorescent and ionic compounds, soluble in water or acid solutions. Some water insoluble compounds are the phosphates and -ites²⁵, arsenates and -ites²⁶ and their derivatives, the molybdates²⁸, the trioxide, the peroxide, the alkali diuranates, and the iodate²⁹, which is slightly soluble in water. All of these are soluble in mineral acids. The phosphates dissolve readily in excess phosphoric acid due to complex formation, but reprecipitate upon dilution^{25b}. Uranyl nitrate hexahydrate³⁰, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, is soluble in polar organic solvents and extraction of the uranyl nitrate from aqueous nitrate solutions affords an excellent separation and purification process (see below).

In the absence of the stronger complexing agents, uranyl ion precipitates as $\text{UO}(\text{OH})_2$ at about pH 4. In presence of ammonium or alkali hydroxides, the diuranate, $\text{H}_2\text{U}_2\text{O}_7$, appears as a yellow gelatinous ppt. Polyuranates with as high as six U atoms per alkali metal atom have been reported³¹. The peruranates of the alkalis are water soluble and form highly colored deep orange solutions when hydrogen peroxide is added to an alkali diuranate suspension³¹.

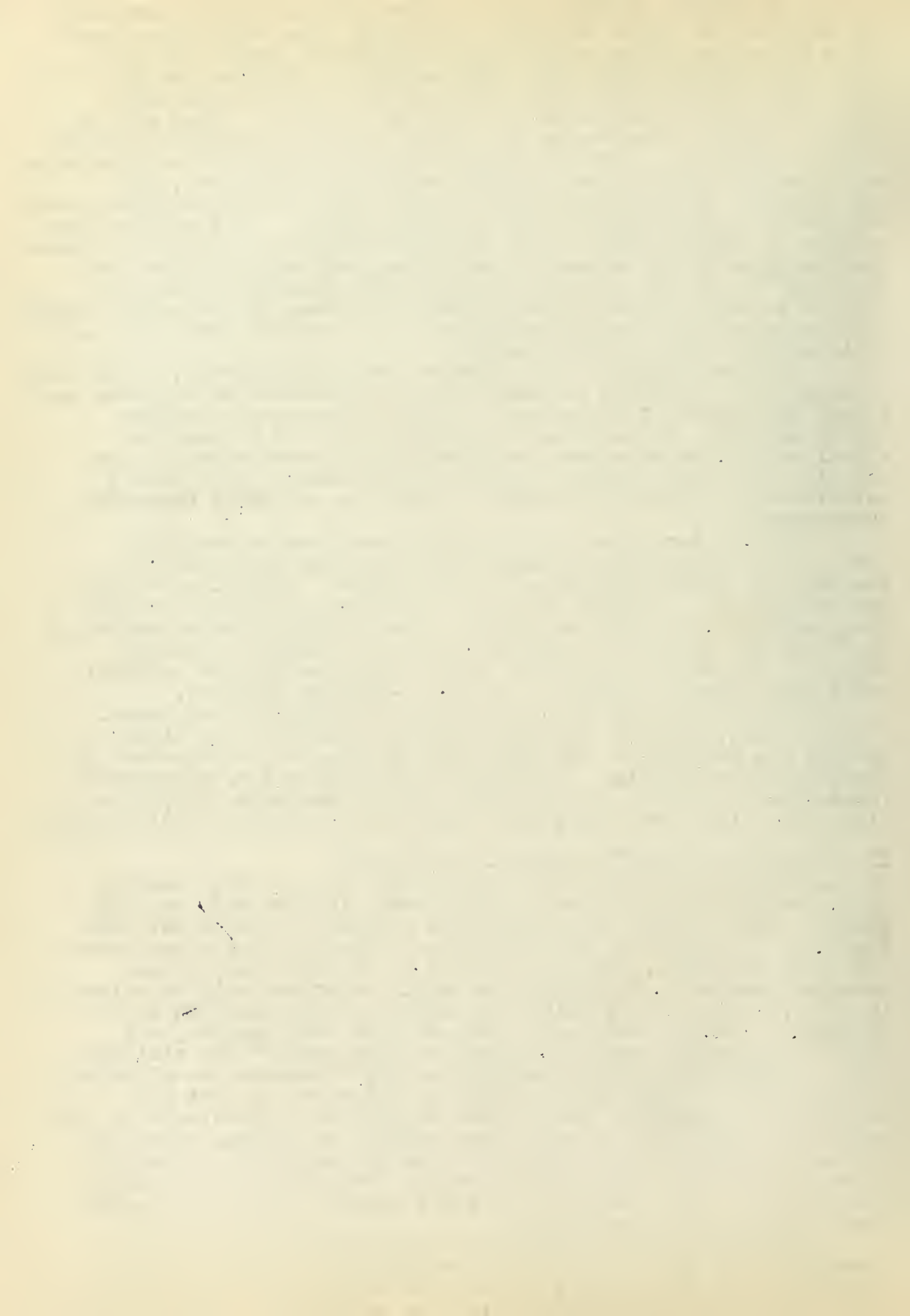
Uranyl ions show an appreciable tendency to complex. Inorganic ions known to complex with it are the carbonate ion, forming e.g. $(\text{NH}_4)_4 \text{UO}_2(\text{CO}_3)_3$ ³², the cyanate, $\text{UO}_2(\text{CNO})_4^{2-}$, and the thiocyanate. Sulfate, fluoride and phosphate appear to form weak complexes in acidic solutions. Some organic groups complexing UO_2^{++} are the acetate, ascorbate, citrate, lactate, malonate, oxalate, salicylate and tartrate ions. The ascorbic and salicylic acids form colored complexes, as does 8-hydroxyquinoline.

5. COMPOUNDS WITH TWO VALENCE STATES OF URANIUM are known. They are U_3O_5 , $\text{U}_3\text{O}_7(?)$, U_3O_8 and $\text{U}_2\text{O}_3\text{P}_2\text{O}_7$ (possibly the binary halides UF_5 and UCl_5). The structure of U_3O_8 can be expressed as $\text{UO}_2 \cdot \text{UO}_2 \cdot \text{UO}_3$ or $\text{U}(\text{UO}_4)_2$. Ignition of yellow uranyl pyrophosphate, $(\text{UO}_2)_2\text{P}_2\text{O}_7$, or of the green uranous oxypyrophosphate, $(\text{UO})_2\text{P}_2\text{O}_7$ yields the light green $\text{U}_2\text{O}_3\text{P}_2\text{O}_7$, which can be written $(\text{UO})(\text{UO}_2)\text{P}_2\text{O}_7$.

II. METHODS OF SEPARATION APPLIED TO URANIUM

A. PRECIPITATION METHODS Where possible uranium is usually precipitated as the diuranate with ammonia (preferred), or with sodium. This affords separation from elements which do not form insoluble hydroxides or are amphoteric. Pyridine and other amines have also been used. Uranyl ions may be precipitated as the ammonium phosphate, $\text{UO}_2\text{NH}_4\text{PO}_4$, in acidic solutions with pH values as low as 1.5 to 2. The uranium phosphates are insoluble in basic solutions, whereas some, e.g. those of iron and aluminum, are soluble. Arsenates and the organic arsenic acids²⁶ are similarly used. 8-Hydroxyquinoline precipitates UO_2^{++} between the pH values of 4 and 12³³. Cupferron precipitates quadrivalent, but not hexavalent, uranium³². The uranous cupferride is insoluble in 2-3N sulfuric or hydrochloric acids, but soluble in organic solvents. Tetravalent uranium precipitates as the hydrous oxide in neutral or basic solutions, forms very insoluble phosphate and arsenate precipitates. The precipitates with fluoride, oxalate and iodate ions which are acid insoluble.

B. COMPLEX FORMATION applied to precipitation separations are exemplified by the uranyl carbonate-complex³⁴ soluble in basic solution, and which serves to separate uranyl ions from the metallic ions which form insoluble hydroxides or carbonates. The complex-



forming organic acids are not of much importance since they complex most other transition elements also.

C. EXTRACTION METHODS were applied by Manhattan Project workers to the separation and purification of uranium in large amounts, and, as stated in the "Synth Report", at a purity seldom attained previously even in the laboratory. The species extracted by this process was uranyl nitrate³⁰, which extracts from concentrated nitrate salt solutions into the more polar organic solvents, such as ethers, ketones and alcohols, and can be removed from these solvents by washing with water. The method was originally applied by Hecht and Grunwald³³ who extracted uranyl nitrate from saturated ammonium nitrate solutions with ether. Nitrate salts other than ammonium may be used as saturating agents, the efficiency of extraction (i.e. the distribution coefficient) varying greatly with the salt used, but for each salt increasing exponentially with increasing nitrate concentration and decreasing with increasing temperature.

Some inner-complexes of uranium are soluble in non-polar organic solvents. Examples are uranyl 8-hydroxyquinoline³⁷, uranyl dibenzoylmethane³⁴ and uranous cupferride³².

D. VOLATILIZATION METHODS can be used to separate uranium from ores and various solids through formation of the volatile uranium hexafluoride. The solid may be first treated with hydrogen fluoride at 400 to 600° to remove silica and then fluorinated with fluorine gas at 200-250°, converting the uranium to UF_6 which is collected in a cold trap.

E. ELECTROLYTIC METHODS find applications in analytical separations. Many metals, e.g. iron and copper are deposited at a mercury cathode while uranium is not.

F. ION EXCHANGE has been used to separate large amounts of uranium from small amounts of fission products. Uranium (uranyl) is loosely held on the resin while the fission products are more strongly held.

IV ANALYTICAL DETERMINATION OF URANIUM

A. GRAVIMETRIC METHODS depend upon the precipitation reactions discussed above. The most widely used involves precipitation, with slight excess ammonium hydroxide, of $(NH_4)_2U_2O_7$ and subsequent ignition to U_3O_8 . Care must be taken to have carbonate ions absent. The precipitates of the ammonium phosphate (at pH2) and the arsenate, though quantitatively insoluble, are fine and somewhat difficult to filter. The phosphate can be ignited (with care to prevent reduction) to the pyrophosphate. The arsenate has the advantage of igniting to U_3O_8 ²⁶. Uranyl 8-hydroxyquinolate, $UO_2(Orine)_3$, is precipitated from acetate buffered solutions³⁵. It dries at 110° to give the trioxinate, but at 200° the digginate, $UO_2(Orine)_2$, is formed and can be weighed in either form³⁵ or ignited to U_3O_8 . Uranous cupferride, $U(cup)_4$, can also be ignited to the oxide U_3O_8 .

B. VOLUMETRIC METHODS^{26,31}. Uranium may be reduced from the uranyl to the uranous (+4) state by means of the zinc (Jones reductor), cadmium and silver reductors or with an aluminum coil. The uranous solution can then be titrated with standard ceric, permanganate, dichromate or ferric solutions. If the uranium is precipitated with 8-hydroxyquinoline, it may be determined by means of the bromine - 8-hydroxyquinoline reaction and titration²⁸.

C. COLORIMETRIC METHODS are used to detect and determine low concentrations of uranium. Some reagents which form colored complexes are ferrocyanides, ascorbic acid, salicylic acid and 8-hydroxyquinoline³⁶. The soluble alkaline peruranates allow a rather sensitive determination. There are many interfering ions in most of these colorimetric methods and preliminary separations are usually necessary.

D. SPECIAL METHODS. Traces of uranium of the order of 1 ppm or less can be detected and determined by the strong fluorescence that traces of uranium impart to certain solids³⁷. For this, the uranium sample is fused with NaF and the resulting cooled disk compared with known standards under ultraviolet light.

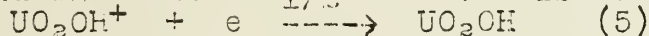
The radioactivity of uranium can serve to indicate its concentration. The radioactivity of solutions can be measured directly using special counting devices, or a known amount of the solution may be evaporated on a disk and then counted. The concentration of uranium in powdered solids may be compared by the ratios of their alpha counts, providing the solids have approximately the same composition. Different elements have different stopping power for radioactive particles.

Uranium has been determined spectrographically, but its spectrum is dense and has very many lines³⁷.

E. POLAROGRAPHY OF URANIUM

Kolthoff and Harris^{38,39,40} have recently studied the polarography of uranium in detail. The reductions were found to differ with the acidity of the solution and the anions present. At all acidities the half-wave potential, $E_{1/2}$, of the first wave was found to be -0.18 volt (vs. S.C.E.), corresponding to a one-electron, hydrogen ion independent reduction of the uranyl ion and postulated as $UO_2^{++} + e \rightarrow UO_2^+$ (1) the remainder of the current-voltage curve varies with the acid concentration. In slightly acid solutions (0.01 to 0.2 N HCl) a second wave with $E_{1/2}$ of -0.92v was obtained of twice the height of the first and corresponding to two one-electron reductions at approximately the same potential, i.e. $UO_2^+ + e \rightarrow UO_2$ (2) (the UO_2 then redissolves $UO_2 + 2H^+ \rightarrow UO^{++} + H_2O$) $UO^{++} + e \rightarrow UO^+$ (3)

In neutral or basic solution the hydrolysis of uranyl ions must be considered. $UO_2^{++} + H_2O \rightleftharpoons UO_2OH^+ + H^+$ (4) The two species of U(+6), i.e. UO_2^{++} and UO_2OH^+ do not reduce at the same potential, so in this case the first wave is again due to (1), but the second wave with $E_{1/2}$ at -0.6v is due to (5) and (2).



The UO_2 formed in (2) and the UO_2OH from (5) do not redissolve in neutral or basic solutions, hence the reduction actually proceeds only to a mixture of quadrivalent and pentavalent uranium.

In strongly acid solutions, e.g. 1M HCl, the relative magnitudes of the two waves change but their sum is unaffected. Apparently a disproportionation of the pentavalent uranium ion, UO_2^+ , occurs. $2 UO_2^+ + 2H^+ \rightarrow UO_2^{++} + UO^{++} + H_2O$ (6) For strongly acid solutions the waves observed are thus explained by reactions (2), (6), and (3). The results of Heal⁴¹ are in substantial agreement with those presented here.

For analytical purposes it is recommended³⁸ that the first diffusion current be measured at -0.5 v vs. S.C.E. in 0.01 to 0.1M HCl with $10^{-4}\%$ thymol present to eliminate the maximum. The diffusion current is proportional to uranyl ion concentration in the range 5×10^{-4} to 4×10^{-3} M. Use can be made of the catalytic effect of uranyl ion on the polarographic reduction of nitrate ion. An empirical procedure was developed which allows polarographic determinations in the range of 2×10^{-7} to 3×10^{-5} M uranium concentration.

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HYDRAZINE DERIVATIVES OF CARBONIC ACID

Edward F. Elslager

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I. Hydrazine System of Compounds

Hydrazine may be considered the parent solvent of a hydrazine system of compounds, just as water and ammonia are regarded as parent solvents (1). The hydrazonium ion, $N_2H_5^+$, is the bearer of acidity in hydrazine from the Bronsted point of view; salts of hydrazine act as acids when dissolved in anhydrous hydrazine. Solvo-bases such as the metallic hydrazides have also been prepared (2).

The use of anhydrous hydrazine as a reaction medium is curtailed largely because of the hardships encountered in its preparation and handling.

II. Solvent Properties of Anhydrous Hydrazine and Reactions Therein.

Anhydrous hydrazine has been found to be a suitable solvent for both organic and inorganic compounds (32). It exists in the liquid state over a convenient temperature range; it is believed to be an associated solvent; it has an exceptionally high dielectric constant in comparison with ammonia. Both hydrazine hydrate and anhydrous hydrazine are very susceptible to oxidation, a reaction which is catalyzed by metallic ions.

Sodium derivatives of hydrazine are readily prepared by the action of anhydrous hydrazine on sodium amide or metallic sodium. Metallic sodium will precipitate metallic cadmium, iron, and zinc from solutions of their salts in anhydrous hydrazine; magnesium, calcium, and barium are not precipitated. Zn, Cu, Al, and Sn do not react with anhydrous hydrazine, although Mg, Ca, and Li show a slight action.

Iodine and sulfur are very soluble; the solubility of halogen compounds in a given series increases as the atomic weight of the halogen increases. Carbonates are insoluble or only slightly soluble in anhydrous hydrazine, while nitrates and ammonium compounds are all soluble with the exception of tertiary ammonium phosphate.

Two hydrazinates of calcium azide have been isolated by Dresser and Browne (10). They are the dihydrazinate, $Ca(N_3)_2 \cdot 2 N_2H_4$ and the monohydrazinate, $Ca(N_3)_2 \cdot N_2H_4$, both prepared in anhydrous hydrazine. Hydrazine azide monohydrazinate, $N_2H_5N_3 \cdot N_2H_4$ has also been prepared (11).

III. Classification of Hydrazine Derivatives of Carbonic AcidA. Non-cyclic Compounds

1. Hydrazinocarbonic Acid (Carbamic acid or N-amino carbonic acid) This compound is the first product in the progressive-hydrazinolysis of carbonic acid (29). NH_2NH_2 is prepared by passing CO_2 gas into cold concentrated hydrazine hydrate; the acid separates out of solution. Its copper and nickel salts have been prepared, as well as zinc carbamate dihydrazinate. Esters of carbamic acid are prepared by an indirect method; for example, the methyl ester hydrochloride, $NH_2NHCO_2CH_3 \cdot HCl$, is prepared from methyl chloro-carbonate and hydrazine hydrate.

Sulfonyl chloride reacts with carbamic acid or its hydrazine salts to give sulfonyl dihydrazide, $SO_2(NHNH_2)_2$.

2. Carbohydrazide

$\begin{array}{c} \text{NHNH}_2 \\ \diagup \\ \text{CO} \\ \diagdown \\ \text{NHNH}_2 \end{array}$ Carbohydrazide, or s-diaminourea, is the dihydrazide of carbonic acid. It was first prepared by Curtius (6) in 1894; hydrazine hydrate and diethylcarbonate were heated in a sealed tube at 100°C.

It may also be synthesized by heating the hydrazine salt of carbazic acid at 140° for 20 hours. Diphenylcarbohydrazide is prepared from diphenyl carbonate and phenylhydrazine; thio-carbohydrazide is produced in the reaction between CSCl_2 and hydrazine hydrate.

Carbohydrazide is used to characterize aldehydes and ketones, reacting with two moles of benzaldehyde forming the dicarbohydrazone, $\text{CO}(\text{NHN}=\text{CHPh})_2$. Curtius prepared carbonyl azide, N_3CON_3 , by slowly diazotizing a concentrated aqueous solution of carbohydrazide hydrochloride.

3. Semicarbazide

$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{CO} \\ \diagdown \\ \text{NHNH}_2 \end{array}$ Semicarbazide is both an amide and a hydrazide of carbonic acid. Thiele (31) prepared it by allowing potassium cyanate to react with hydrazine sulfate which had been neutralized with sodium carbonate; it was isolated as the benzaldehyde derivative. The partial hydrolysis of aminoguanidine in sodium carbonate solution and the sealed tube reaction of urea and hydrazine hydrate also yield semicarbazide. Free semicarbazide (3) can be prepared by adding semicarbazide sulfate to liquid ammonia. Treatment of the sulfate with aqueous $\text{Ba}(\text{OH})_2$ yielded 80% of the desired product.

Semicarbazide is stable in dilute acids, but is hydrolyzed by strong alkali or acids to CO_2 , N_2H_4 , and NH_3 . Boiling water yields $(\text{NHCONH}_2)_2$ and hydrazine. Semicarbazide has been widely used in the characterization of carbonyl compounds. The more negative the groups attached to the carbon adjacent to the carbonyl, the more difficult it is to form the semicarbazone (20).

4. Aminoguanidine

$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{C} \text{ NH} \\ \diagdown \\ \text{NHNH}_2 \end{array}$ This compound may be prepared from nitroguanidine by reduction with zinc dust, with metallic sodium in liquid ammonia, or by catalytic hydrogenation using Adams' catalyst. Pellizzari treated cyanamide with hydrazine sulfate; the reaction of cyanamide with hydrazines is general for the preparation of monosubstituted aminoguanidines. Aminoguanidine may also be prepared by the hydrazinolysis of nitrosoguanidine.

Aminoguanidine is a stronger base than hydrazine. By hydrolysis, it is converted to semicarbazide. Its reactions with nitrous acid are varied: in strong mineral acid, guanylazide is formed; (the latter may cyclize to amino-tetrazole); in neutral solution, 1-guanyl-4-nitrosoaminoguanyltetrazene is formed; in acetic acid solution, ditetrazoyltriazene is the product. Aminoguanidine reacts with carbonyl compounds with the elimination of water.

5. Diaminoguanidine and Triaminoguanidine

$\begin{array}{c} \text{NHNH}_2 \\ \diagup \\ \text{C} \text{ NH} \\ \diagdown \\ \text{NHNH}_2 \end{array}$ Diaminoguanidinium chloride, or bromide, is prepared by reacting cyanogen chloride or bromide with hydrazine. It has been obtained from the reaction of hydrazine hydrate with dicyandiamide and by the reduction of nitroaminoguanidine with zinc dust (30).

Triaminoguanidine can be prepared by refluxing carbon tetrachloride with hydrazine hydrate. It is synthesized from diaminoguanidine, aminoguanidine, or guanidine by the action of 1,2, or 3 moles of hydrazine hydrate, respectively.

B. Cyclic Compounds

1. Introduction-Cyclic structures for benzene, pyridine, etc. are well established in organic chemistry; inorganic cyclic structures include silica, sulfur, phosphonitric chlorides, the metaphosphates, sulfur trioxide, etc. The cyclic compounds of nitrogen containing the -NHNH- group will be considered cyclic derivatives of the straight chain inorganic compound hydrazine; the -CO- group is derived from carbonic acid; in addition, any of these groups may be substituted.

2. Azoles and Related Systems - The ending-azole designates a five membered ring containing two or more hetero atoms, one of which is nitrogen.

a) General Preparations

1) The azoles may be prepared from the 1,4-dienol compounds (19); for example, a diacetylhydrazide, $(\text{RCO-NH})_2$, may be converted by the action of P_2S_5 to a 1,3,4-thiadiazole (9). 2) These compounds may be synthesized from α -substituted aldehydes and ketones. For example, formyl hydrazide, HCOH_2N_2 , condenses with itself to form an amino triazole.

3) A third synthesis involves the addition of diazo compounds and azides to double and triple bonds. Pyrazole can be prepared from acetylene and diazomethane (19).

4) Azoles may be prepared from hydrazines. Hydrazine adds across the triple bond of propargyl diethylacetal, $\text{HC}\equiv\text{CCH}(\text{OEt})_2$, forming dihydropyrazole by the elimination of two molecules of ethanol.

5) The azolones are carbonyl derivatives of the azoles; they are prepared in a manner similar to the azoles, but the aldehyde or ketone group in the starting material is replaced by an acid or ester group. The combination of addition and condensation that hydrazine undergoes with acrylic acid parallels the reaction of propargyldiethylacetal above.

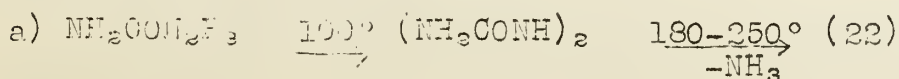
b) Chemical Properties of the Azoles

The chemical and physical properties of the azoles are largely a resultant of the effects of the groups present in the ring and resonance which gives stability to the ring structure. Substitution will occur on the ring but is not common. Addition reactions include ordinary reduction and additions to the amono-aldehyde system. The azoles are bases of varied strength; they form salts with acids and react with alkyl halides to form quaternary salts.

Azole rings can be opened by benzoyl chloride and alkali, reductive cleavage, and acid reduction yielding degradation products which prove useful in structure determination (19).

1. Some Important Azoles

1. Hydrazide (1,3,4-triazole-3,5-dione). $\begin{array}{c} \text{NH} \quad \text{NH} \\ \diagdown \quad \diagup \\ \text{OC} \quad \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \\ | \\ \text{H} \end{array}$ is prepared by one of the following reactions:

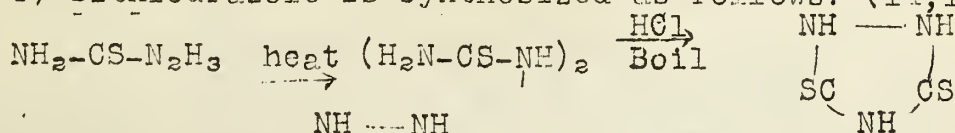


c) . It gives a red color with ferric chloride, indicating that some tautomerism exists. It reduces ammoniacal silver nitrate in the cold.

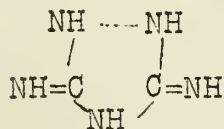
d) Phosphorus pentasulfide converts urazole to 1,2,4-triazole (23)

e) Iminourazole, which represents an intermediate compound between guanazole and urazole, can be obtained by the action of urea on aminoguanadine hydrochloride, or by the interaction of dicyanodiamidine hydrochloride on hydrazine hydrochloride (24).

f) Dithiourazole is synthesized as follows: (14,13)



2. Guanazole



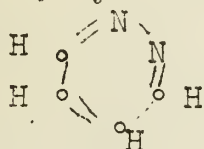
a) Guanazole is readily prepared by heating hydrazine hydrochloride and dicyanodiamide in alcohol at 100°.

b) Nitroso guanazole, phenyl guanazole, phenylmethyl guanazole, and many other aromatic derivatives have been prepared (25); the sulfate, nitrate, picrate, silver nitrate salt, mercuric chloride salts, and guanazole copper sulfate have been synthesized.

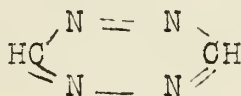
c) In recent years, condensation products of guanazole and its derivatives with aldehydes and ketones have become commercially important as resins, and paint and varnish modifiers (7).

3. The Azines and Related Compounds - Azines are six membered rings containing two or more heteroatoms, one of which is nitrogen.

A. Pyridazine - Pyridazine is prepared by the condensation of hydrazine and α -ketoglutaric acid, followed by bromine oxidation, decarboxylation, treatment with POCl_3 , and action of HI.



B. Tetrazines



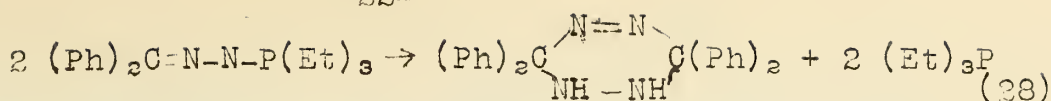
1. Preparations

a) From thioamides (18) Alc
 $2\text{R.CSNH}_2 + 2\text{H}_2\text{H}_4 \xrightarrow{\text{Reflux}} 2\text{H}_2\text{S} + 2\text{NH}_3 + \text{RC} \begin{array}{c} \text{NH-NH} \\ \diagup \quad \diagdown \\ \text{N} \text{---} \text{N} \end{array} \text{CR}$

b) Diazoacetic acid undergoes dimerization with strong alkali or ammonia to a dihydro product, which by oxidation yields the 3,6-dicarboxylic acid of 1,2,4,5-tetrazine. Free tetrazine is prepared by carefully heating a mixture of the tetrazine dicarboxylic acid and sand at 160° (5).

c) The interaction of sulfur monochloride and organic acid anides is a convenient way to prepare various thiotetrazine derivatives. (21).

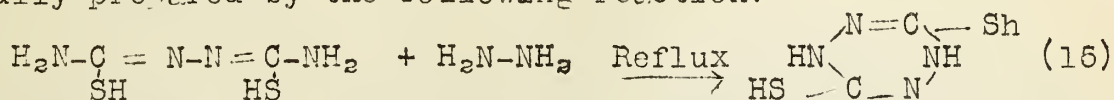
d) Tertiary phosphines add directly to various aliphatic diazo-compounds forming phosphazines: $\text{R}_2\text{C}=\text{N}_2 + \text{P R}_3 \rightarrow \text{R}_2\text{C}=\text{N}-\text{N}=\text{P R}_3$. The phosphazines readily hydrolyze into hydrazones and phosphine oxides, but in benzene or chloroform, the hydrolysis occurs as follows:



e) The reduction and subsequent cyclization of various phenylhydrazones yields tetrazines (17):

f) Various tetrazine derivatives have been prepared by the action of hydrazine hydrate on α -hydroxy acids (8).

g) Thioamono tetrazine derivatives have been successfully prepared by the following reaction:



2. Properties of Free Tetrazine

Free tetrazine is an interesting compound. It is crimson in color, and melts at 99° to a purple-red liquid. Liquid ammonia maintained at temperatures below -40° is the only solvent from which tetrazine has ever been recovered. From other solvents, the solute is volatilized with the solvent. In liquid ammonia, concentrated solutions are dark brown, intermediate ones blood red, and dilute solutions are pale buff (33).

Tetrazine reacts with aqueous solutions of HgCl_2 , AgNO_3 , AuCl_3 , and H_2PtCl_6 without the formation of definite salts or addition products; the salt is often reduced to the free metal.

3. Uses

Recently, resinous condensation products of diaminotetrazine and aldehydes have been investigated as plastics for molding and impregnating processes (26).

C. p-Urazine, $\text{OC} \begin{array}{c} \text{NH}-\text{NH} \\ \text{NH}-\text{NH} \end{array} \text{CO}$, hexahydro-3,6-diketo-1,2,3,6-tetrahydrotetrazine.

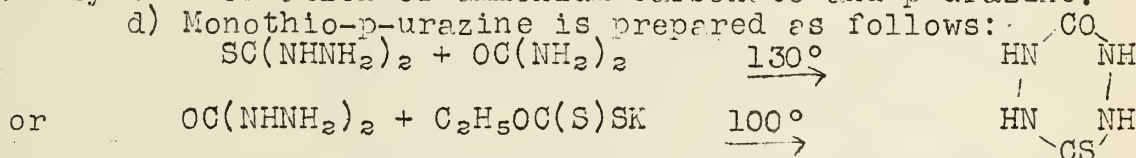
1. Preparation

a) p-urazine is obtained in 80% yield by the action of three moles of NaOBr on two moles of semicarbazide (16).

b) Ethyl hydrazine dicarboxylate, $\text{N}_2\text{H}_2(\text{CO}_2\text{Et})_2$, is prepared by heating an alcoholic solution of ethyl chloroformate with hydrazine hydrate; p-urazine is obtained when this compound is heated with two moles of hydrazine hydrate in a sealed tube (4).

c) When N,N' -dichlorourea is treated with ammonia, hydrolysis occurs, accompanied by the liberation of nitrogen and by the formation of ammonium carbonate and p-urazine.

d) Monothio-p-urazine is prepared as follows:

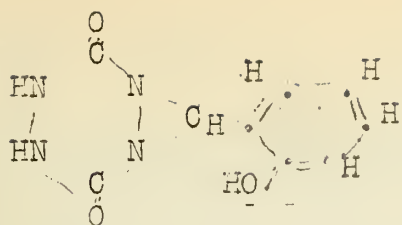


Dithio-p-urazine hydrochloride is prepared by refluxing dithiohydrazodicarbamide with alcoholic hydrazine hydrate. Dithio-p-urazine is readily obtained from the hydrochloride by treatment with barium hydroxide.

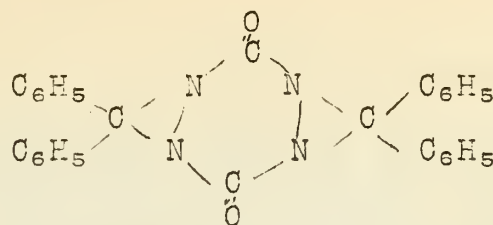
2. Reactions of the Urazines

a) Hydrolysis of p-urazine can be easily effected by heating it with concentrated sulfuric acid at 130° . Carbon dioxide is rapidly evolved, and hydrazine sulfate crystallizes out on cooling.

b) p-urazine (1 mole) reacts with aldehydes (1 mole) or ketones (2 moles) to form bi- and tri-cyclic compounds:



Salicylidene-p-urazine



dibenzophenone-p-urazine

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Glendall L. King

October 19, 1948

Introduction and Historical. (A1, A2). The odor arising from freshly prepared ozone had long been known. However, it was first really investigated by the Dutch chemist Van Muren, who, about eleven years after the discovery of oxygen, demonstrated that oxygen which had been subjected to an electric discharge has a peculiar odor. Cruikshank, in 1801, noticed the same characteristic odor about the anode during the electrolysis of water.

Schonbein, in 1840, noted this property in air subjected to the silent electric discharge, in oxygen generated by the electrolysis of water, and in the slow combustion of phosphorus in air. He gave to the new gas the name ozone, from the Greek, meaning "to smell". This investigator first noted that ozone is a distinct form of matter and to him goes the honor of having discovered it.

By making use of the fact that certain essential oils (cinnamon and turpentine) absorb ozone without taking up any appreciable quantity of oxygen, Soret, about 1866, demonstrated that ozone is O_3 . The loss of volume through adsorption of ozone from ozonated oxygen was twice that observed in the original ozonation of the gas. It was therefore inferred that three volumes of oxygen are condensed to produce two volumes of ozone.

II. Preparation. Ozone has been prepared by (a) chemical action such as the gentle heating of certain oxygen containing compounds, (b) the electrolysis of dilute sulfuric acid, (c) silent electric discharge in air or oxygen, (d) ultraviolet irradiation of oxygen, (e) introduction of a heated spiral of platinum wire into liquid oxygen, and (f) exposure of moist phosphorus to the air.

Only one method of electrolytically producing ozone will be discussed. Recent investigation (1) has shown that ozone can be prepared efficiently by electrolysis of perchloric acid at low temperatures. Electrolytic ozone, free of oxides of nitrogen and other impurities, was obtained directly at concentrations above 20 weight-per cent. The authors found that the absolute pressure over the electrolyte can have a marked effect on current efficiency, as improved ozone yields were obtained at absolute pressures of 0.1 atmosphere. Eutectic mixtures of perchloric acid and water gave excellent results at temperatures below $-50^{\circ}C$. Sodium and magnesium perchlorates may be added to perchloric acids solutions to give slightly lower melting points, with indication of some increase in current efficiency. Smooth platinum was found to be a satisfactory anode material and silver-free lead is suitable for the cathode. The combined mechanical and chemical loss of perchloric acid is less than 1.7 grams per kilogram of ozone.

A comparison of perchlorate electrolytic ozone with silent discharge ozone follows:

<u>Perchlorate Electrolytic Ozone.</u>	<u>Silent Electric Discharge Ozone</u>
1. Product contains only oxygen and hydrogen as impurities	1. Oxides of nitrogen impurities result when air or nitrogen containing oxygen is used.
2. Energy yield increases with increase in ozone concentration.	2. High ozone yields only when the ozone concentration is low.
3. Raw material is distilled water.	3. Several hundred to several thousands pounds of air must be passed through apparatus per pound of ozone produced.

III. Structure. Many conflicting statements may be found in the literature concerning the structure of the ozone molecule. However, it may be said that spectroscopic data have been interpreted in recent years as showing that the ozone molecule consists of two oxygen atoms close together, and a third one farther away and equidistant from the first two. This structure could be described as that of an oxygen molecule with a third oxygen only loosely bonded to it.

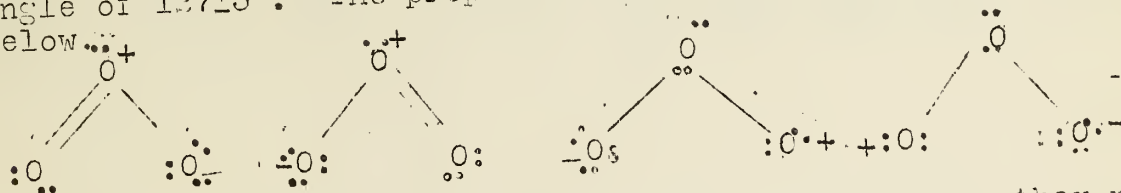
Gerhard (2) made a thorough study of the infrared spectrum of ozone and claims that the molecule can not be absolutely linear or be represented by an equilateral triangle. He suggested that the molecule could be best represented by an isosceles triangle in which the angle at the apex was less than 60° . Badger and Bonner (4) then reviewed the infrared data of Gerhard and suggested that the structure of ozone was similar to that of sulfur dioxide as suggested by Mecke (3). That author had given an analysis of the SO_2 bands compatible with an apex angle of about 120° . Benedict (6), independently, came to the same conclusion as Badger and Bonner from a reexamination of Gerhard's results.

Soon thereafter, Hettner and others (5) examined again the infrared spectrum of ozone and suggested that the ozone structure was that of an isosceles triangle with a vertex angle of 39° .

Mulliken (7) reviewed the infrared data concerning ozone structure and supported the acute angled model as "very probably correct". Relying heavily upon the work of Hettner et al, Mulliken proposed a structure of the type O_2O^+ , the apex atom being O^+ . In this type of structure an O-O distance of 1.12 Å was assumed for the two base atoms, which with an apex angle of 39° gave the other O-O distance as 1.68 Å. On the basis of these assumptions, Mulliken postulated an electron configuration corresponding to O_2O^+ . Such a structure should have a large permanent dipole, whereas only a rather small one was observed by Lewis and Smyth (8), but since this result was obtained in oxygen solution it was not conclusive.

Since that time other spectroscopic data have been obtained in support of the acute angle model (9), but again the same data were said to support the obtuse angle model equally well (10).

An electron diffraction investigation of ozone by Shand and Spurr (11) showed that the molecule is in the form of an isosceles triangle with O-O bond distance 1.26 ± 0.02 Å and O-O-O angle of $127 \pm 3^\circ$. The proposed resonating structures are listed below.



Other singly bonded structures are neglected because they place a double positive formal charge on the central oxygen, and the structure involving two double bonds would put ten electrons on the central oxygen atom.

Pauling (12) believes that the Structure of ozone as proposed by Shand and Spurr is the correct one, although he does admit that it is difficult to understand the contradictory conclusions reached by spectroscopic investigators.

IV. Reactions and uses. Although the reactions of ozone will not be discussed in any detail, a few typical reactions are summarized below:

<u>Material treated with ozone</u>	<u>Product</u>
1. iodide	1. iodine
2. Cobalt (II) and Nickel (II)	2. Cobalt(III) and Nickel(III)
3. Thallium (I)	3. Thallium (III)
4. Tin (II)	4. Tin (IV)
5. Iron (II)	5. Iron (III)
6. Chromium (III)	6. Chromates or dichromates
7. Sulfides (of Pb, Cu, Zn, Cd)	7. Corresponding sulfates
8. Hydrogen sulfide	8. Water and sulfur
9. Sulfur dioxide	9. Sulfur trioxide
10. Selenites and Tellurites	10. Selenates and Tellurates
11. Nitrite	11. Nitrate
12. Hypophosphites and phosphites	12. Phosphates

Some of the main uses of ozone are;

1. Purification of water.
2. Deodorizer in public places.
3. Bleaching agent for fibers, furs, wood pulp, oils, fats, and waxes.

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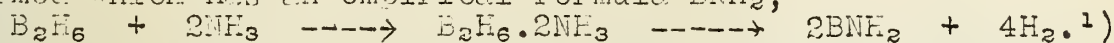
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Paul H. Mohr

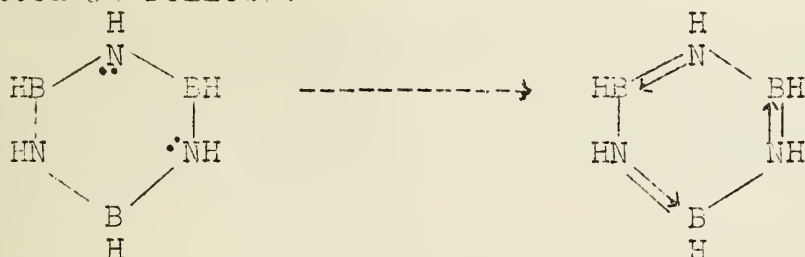
October 19, 1948

One of the most interesting advances of inorganic chemistry into what may be considered the realm of organic chemistry has been the discovery of compounds containing boron-nitrogen linkage. Many interesting analogies have been found where this linkage has replaced a carbon to carbon bond.

Probably the most striking of these compounds is borazol. When the 2-ammoniate of diborane is decomposed thermally, a liquid is formed which has an empirical formula BNH_2 ;



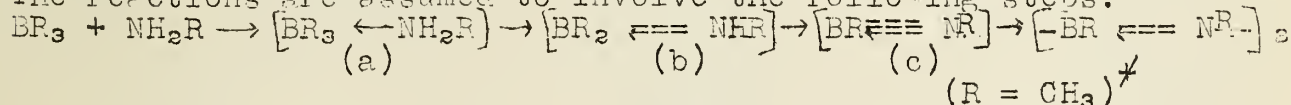
From vapor density measurements it was found that this substance is a trimer, (1). Further investigations of its chemical properties^{1,2)} seemed to show that it possesses a ring structure corresponding to the benzene ring. This hypothesis has been substantiated by electron diffraction studies³⁾ and by a study of the Raman and infra red⁴⁾ spectra. Structurally Borezol may be represented as follows:



Whereas Benzene has a normal covalent bond in its accepted alternating double bond formula, borazol may be considered to have a coordinate bond which resonates in a similar fashion. This coordinate bond is not quite as strong as the covalent bond in benzene as is borne out in its greater reactivity.

Hexamethylborazol

When equimolar quantities of boron trimethyl and methylamine are heated at 450C under a pressure of 20 atmospheres, colorless crystals of hexamethylborazol are formed⁵. This reaction, however, takes place with the formation of a number of intermediate products which may be isolated under the appropriate conditions. The reactions are assumed to involve the following steps:



The isolation of these intermediate products gives proof that the reaction proceeds as suggested.

A. The Formation of $\text{BR}_3 \leftarrow \text{NH}_2\text{R}$

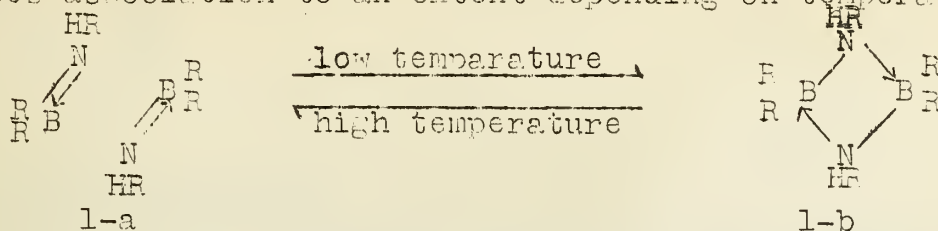
When boron trimethyl is allowed to react with methylamine at the temperature of liquid air, the inorganic ethane type compound $\text{BR}_3 \leftarrow \text{NH}_2\text{R}$ is formed as a white crystalline substance. These crystals have a melting point of 26.4°C , a boiling point of 144°C , and when heated dissociate into the original components.

B. The Formation of $\text{BR}_2 \leftarrow \text{NHR}$

The ethane analogue, $\text{BR}_3 \leftarrow \text{NH}_2\text{R}$ may be converted into the ethylene analogue $\text{BR}_2 \leftarrow \text{NHR}$ in practically 100% yields on heating at 310°C and under a pressure of 20 to 30 atmospheres. Like the organic analogue $\text{CR}_2=\text{CHR}$ it is a low boiling,

*A convenient system of nomenclature has been suggested by Wiberg and Hertwig⁵⁾. Since compound (a) is an inorganic ethane it may be called "borazane". In a like manner compound (b) is called "borazene" and (c) "borazine".

colorless, mobile liquid. It is unsaturated and like the ethylenic compound undergoes polymerization and addition reactions. In the vapor state it is monomeric, in the liquid state it undergoes association to an extent depending on temperature.



Since the equilibrium is established slowly the monomeric vapors can be cooled rapidly to form a metastable monomeric liquid. On standing white crystals of the dimer precipitate from solution. The boiling point of the monomeric liquid is 38.3°C; its organic counterpart, trimethyl ethylene boils at 38.4°C. The dimerization is comparable to the organic ethylenic compounds which dimerize to cyclobutanes.

C. The Formation of $Br \equiv \equiv NR$

The ethylenic compound $BR_2 \equiv \equiv NHR$ may be converted into the acetylenic analogue by heating to a temperature of 450°C. This compound has, however, not been isolated since it is converted immediately into the trimer, hexamethylborazol. Dimethyl acetylene, the organic analog goes over to hexamethylbenzene merely by shaking with sulfuric acid.

Comparison of the Physical Properties of Hexamethylborazol and Hexamethylbenzene.

The physical properties of hexamethylborazol and its organic counterpart hexamethylbenzene show marked resemblances as is evident from the following data.

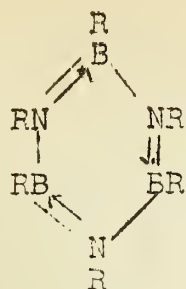
	<u>Hexamethylborazol</u>	<u>Hexamethylbenzene</u>
Molecular weight	164.7	162.3
Crystal Form	colorless broad needles	colorless broad needles
Vapor Pressure (30°)	very low	very low
Boiling point	494°A	537°A
Melting point	370°A	439°A
Heat of Vaporization	11.54 kcal	12.87 kcal
Trouton Constant	23.4	23.9
In Benzene	very soluble	very soluble
In Ether	soluble	soluble
In Water	insoluble	insoluble

Borazol and its mono- to hexamethyl derivatives boil at a somewhat lower temperature than their organic analogues. The

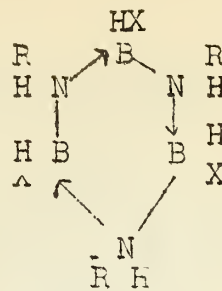
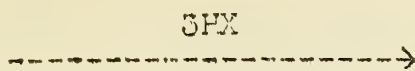
ratio, $\frac{Tb.p. (inorg.)}{Tb.p. (org.)}$, where $T = ^\circ K$, has a constant value of 0.93±.01.

Chemical Properties of Hexamethylborazol

Like borazol itself the hexamethyl derivative is more reactive than its organic analogue. The addition of three moles of HX ($X = Cl$ or OH) takes place slowly at room temperature without the use of a catalyst. The ring network of this cyclohexane analogue is less stable than that of the borazol ring. The ring is now held together by coordinate bonds and consequently breaks down on heating to the monomeric ethylene analogue $BRX \equiv \equiv NHR$



2-a

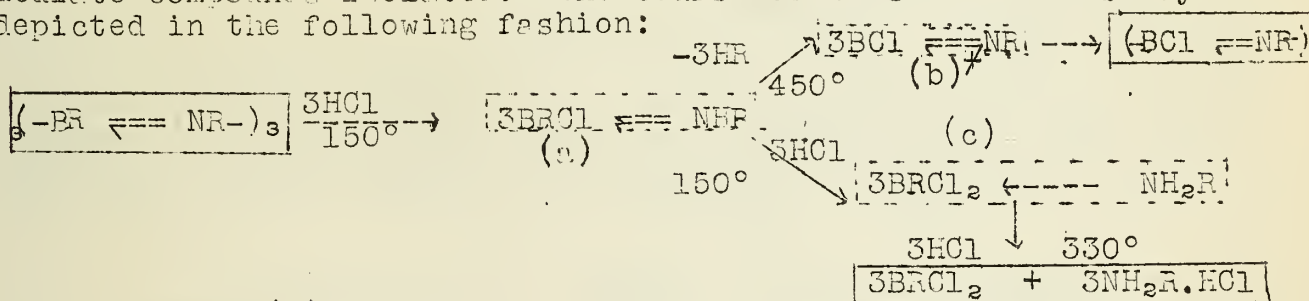


2-b

A. Reaction with HCl

Heating hexamethylborazol with HCl in the molar ratio 1:3 at high temperatures displaces three boron bound methyl groups to form a trichloromesitylene analogue. If an excess of HCl is used a reaction takes place which results in the breaking of all N B ----- N bonds to form three moles of BRCl_2 and $\text{NH}_2\text{R.HCl}$.

This reaction again may be carried out in steps and the intermediate compounds isolated. The course of these reactions may be depicted in the following fashion:



Reaction Step (a)

Addition of HCl to hexamethylborazol, at room temperature or 90° , slowly reacts to form a product of type 2-b. It is a white crystalline addition product which can be looked upon as a trimeric form of $\text{BRCl} \equiv \text{NHR}$. On heating to 150°C this compound melts (somewhat over 125°) and decomposes into an ethylenic type compound $\text{R} \equiv \text{B} \equiv \text{N} \equiv \text{R}$.

In the vapor state at 150°C $\text{BRCl} \equiv \text{NHR}$ is monomeric. At room temperatures a crystalline dimer is formed which sublimes at $40-50^\circ$ under a vacuum.

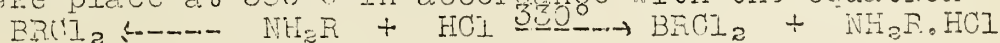
Reaction Step (b)

On heating $\text{BRCl} \equiv \text{NHR}$ at $400-500^\circ\text{C}$ for several hours, one mole of methane is evolved and the acetylenic derivative is formed. This product cannot be isolated and goes directly into the trimeric form, trichlorotrimethyl borazol (inorganic trichlomesitylene).

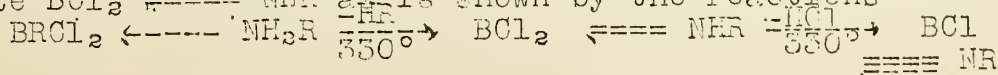
The formation of trichlorotrimethylborazol by this reaction is not a simple one and proceeds in a stepwise fashion by way of an addition compound which decomposes into the "ethylenic" and "acetylenic" compound to finally reunite into the trimer.

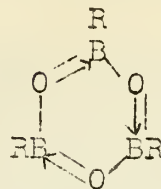
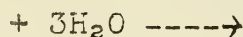
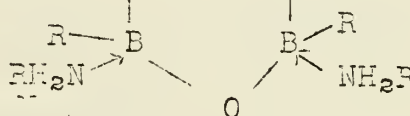
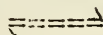
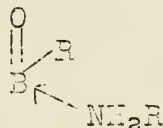
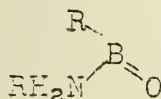
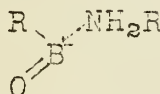
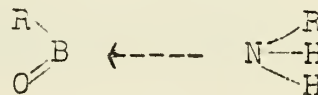
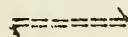
Reaction Step (c)

Like the organic ethylenes, $\text{BRCl} \equiv \text{NHR}$ adds one mole of HCl $\text{BRCl} \equiv \text{NHR} + \text{HCl} \rightarrow \text{BRCl}_2 \text{---} \text{NH}_2\text{R}$. In some respects this compound can be considered to be an addition product of BRCl_2 and NH_2R since decomposition in the presence of HCl does take place at 330°C in accordance with the equation



Reaction step (b) and (c) are generically related by the intermediate $\text{BCl}_2 \equiv \text{NHR}$ as is shown by the reactions



$$\begin{array}{c}
 R \\
 \diagup \quad \diagdown \\
 B \quad \quad NR \\
 \diagdown \quad \diagup \\
 RN \quad \quad BR \\
 \diagup \quad \diagdown \\
 RB \quad \quad N \\
 \diagdown \quad \diagup \\
 \quad \quad R
 \end{array}$$
 $+3\text{NH}_3$
$$(-BR \rightleftharpoons NR)_3 \xrightarrow[R.T.]{3HOH} [3BR(OH) \rightleftharpoons 3NHR] \xrightleftharpoons[R.T.]{\text{tautomerism}} [3BRO \leftarrow 3NH_2R] \xrightarrow[140^\circ]{\text{trimerization}} [3BR(OH)_2 + 3NH_2R.HCl] + (BRO)_3 + 3NH_2R$$
$$\begin{array}{c} \text{R} \\ \diagdown \\ \text{B} \\ \diagup \\ \text{HO} \end{array} \rightleftharpoons \begin{array}{c} \text{R} \\ \diagdown \\ \text{N} \\ \diagup \\ \text{H} \end{array}$$


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William L. Jolly

October 26, 1948

I. Photographic Processing

A. The Theory of Development

1. Physical Development: (5, pp. 306-9), (6, p. 547) (4, p. 82)

A physical developer contains a reducing agent, free silver ions, and a weak acid. The silver which forms the image is not derived from the silver halide of the emulsion. Physical development can be subdivided into pre-fixation development and post-fixation development.

2. Chemical Development: (5, pp. 309-28), (16), (6, pp. 299-304), (17), (3)

The silver bromide grains in the emulsion are reduced, starting from specific points on the surface. The developer does not contain any free silver ions and is a stronger reducing agent than one which acts as a purely physical developer. The hypotheses concerning the mechanism of chemical development fall into two broad groups:

a. Those based on the assumption that the latent-image nuclei serve merely as condensation centers for silver formed by the reduction of silver ions. The latent-image material plays no part in promoting the specific reaction between the developer and silver ions. (This is the classical, yet discredited Ostwald-Abegg hypothesis).

b. Those based on the assumption that the latent-image nuclei in some way act to accelerate the specific reduction of silver ions.

(1) The latent-image nucleus acts as an "electrode" which readily accepts electrons from the developer.

(2) The molecules or ions of the developing agent participate directly in the reduction of the silver ions in contact with the silver nucleus.

B. Chemical Developing Solutions (1), (2), (6, pp. 315-42) (3, pp. 40-51)

1. The Developing Agent:

a. Inorganic: Ferrous oxalate, ferrous fluoride, sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), hydrogen peroxide, hydroxylamine, hydrazine, cuprous chloride.

b. Organic: The Andresen-Lumiere rule states that a reducing agent, to have developing action, must be an aromatic compound comprising one benzene nucleus with not fewer than two hydroxy groups, two amino groups, or one hydroxy and one amino group, in either ortho or para positions. Organic developing agents have been discovered, however, whose molecular structures do not conform with this rule.

2. The Preservative:

All organic developing agents have a strong affinity for oxygen. It is necessary, therefore to add an antioxidant agent, which is usually sodium sulfite or sodium bisulfite. Sulfite performs other functions as well:

a. Protects organic developing agents against aerial oxidation.

b. Prevents the formation of staining developer products by reacting with the oxidized developing agent to form sulfonic acids.

c. Acts as a silver halide solvent by the formation of the complex ion: $\text{Ag}(\text{SO}_3)_2^-$. Thus practical chemical development usually is a "mixed development", in which physical development plays an important part.

d. Sulfite is a weak alkali and under certain conditions increases the rate of development and the maximum density obtainable.

3. The Accelerators (Alkalies)

For any particular developing agent the rate of development is a function of the pH of the solution. The particular alkali appears to be immaterial, so long as the quantity used results in a solution having the same pH value. The alkalies commonly employed are the alkaline carbonates and hydroxides, the basic phosphates, the borates and metaborates.

4. The Restrainer:

The presence of an alkali metal halide, such as potassium bromide, lowers the degree of ionization of silver bromide, and by reducing the concentration of silver cations restrains development.

C. Fixing Solutions (5, pp. 508-38), (6, pp. 352-72), (4, pp. 131-151), (3, pp. 65-74), (2)

Among the many silver halide solvents may be mentioned the sodium, potassium and ammonium thiosulfates and thiocyanates, sodium and potassium cyanides, sodium sulfite, ammonia, thiourea, thiosinamine, and concentrated potassium iodide. Of these, all but the thiosulfates are impractical either because of their high cost, lack of stability, effect on the emulsion or silver grains of the developed image, or poisonous nature. The precise complexing action of thiosulfate in fixing baths is still obscure.

D. Bleaching Solutions:

In reversal processes, it is necessary to remove the initially developed silver image without disturbing the silver halide remaining in the emulsion. Various oxidizing agents employed include: dichromate, ferricyanide, permanganate, and persulfate.

E. Miscellaneous Solutions

1. Reducing (5, pp. 542-58), (3, pp. 85-92), (6, pp. 565-81), (2)
2. Intensifying (5, pp. 542-58) (6, pp. 565-81), (2)
3. Toning (5, pp. 562-80) (3, pp. 108-118) (6, pp. 644-61), (2)
4. Combined Developing and Fixing (21), (19), (18)
5. De-sensitization (3, pp. 61-4), (4, pp. 274-6)
6. Hardening (2), (4, pp. 140-3), (5, pp. 100-126)
(6, pp. 553)

II. Types of Reproduction

A. Negative-Positive Processes

1. Black and White:

- a. Development
- b. Fixation

2. Natural Color: [Gen. references on color phot: {7}{9}]

Three-color color photography has been adopted generally; it is a process the fundamentals of which were first described in 1862 by Ducos du Hauron in France. As early as 1859 Helmholtz established his theory of color vision; in this he assumed that three color-sensitive organs were present in the eye, these organs responding to blue, green, and red light. This theory was confirmed only recently by von Staudnitz (3), who isolated from the retinal cones three colored substances that absorb blue, green, and red light, respectively.

There are two fundamental processes in natural-color photography; the additive process and the subtractive process. The additive process relies on the fact that by mixing blue, green, and red light rays all colors, including white, can be obtained. In the subtractive process, colors are produced by placing filters in the path of a beam of white light produced by a single source. Most modern color processes utilize the subtractive color synthesis. This discussion will be limited to subtractive color processes employing an "integral tripack" (three light-sensitive emulsions coated on a supporting base), as well as to the "dye coupling development" method of coupler formation.

In coupling development, the dye image is usually formed by the coupling (condensation) of the oxidized developing agent with an amine or phenol (the coupler). The coupler may either be incorporated in the emulsion, or it may be introduced in the developing solution.

Processing procedure for films such as Kodacolor (23) and Agfacolor, (7), (20), (22), (24), (15), (12)

- a. Coupling development
 - b. Bleach
 - c. Fixation
- (couplers incorporated in emulsion)

B. Reversal Processes (25),

1. Black and White: (3, pp. 93-97)

- a. First development
- b. Bleach
- c. Exposure
- d. Second development
- e. Fixation (if necessary)

2. Natural Color: (The above remarks under negative-positive color processes apply here also).

- a. Couplers incorp. in emulsion (e.g. Ansco Color (10) (11), Agfacolor, (7), (20), (22), (24), (15), (12) Ektachrome (14).

- (1) First development (black and white)
- (2) Exposure (white light)
- (3) Coupling development
- (4) Bleach (only metallic Ag removed)
- (5) Fixation

- b. Couplers not incorp. in emulsion (Kodachrome). (13)

- (1) First development (black and white)
- (2) Exposure to red light
- (3) Blue-Green image developed in red-sensitive layer

- (4) Exposure to blue light
- (5) Yellow image developed in blue-sensitive layer
- (6) Magenta image developed in green-sensitive layer (fogging development)
- (7) Bleach
- (8) Fixation

Additive Color-System

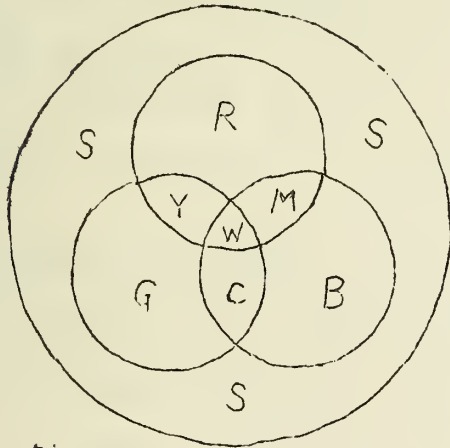
W = white light
S = black

Primary Colors

R = red
G = green
B = Blue

Combinations

$R + G = Y$
 $R + B = M$
 $G + B = C$
 $R + G + B = W$



Subtractive Color-System

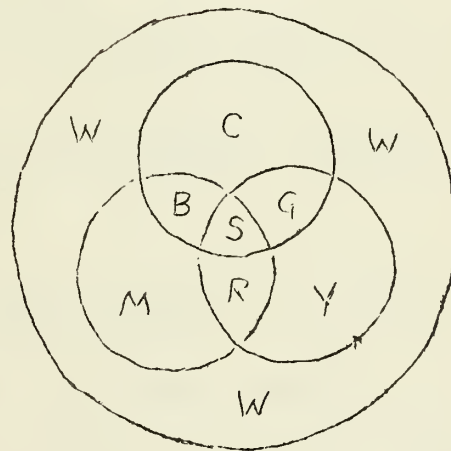
W = white

Primary Minus-Colors

$W - R = C$ = cyan
 $W - G = M$ = Magenta
 $W - B = Y$ = yellow

Combinations

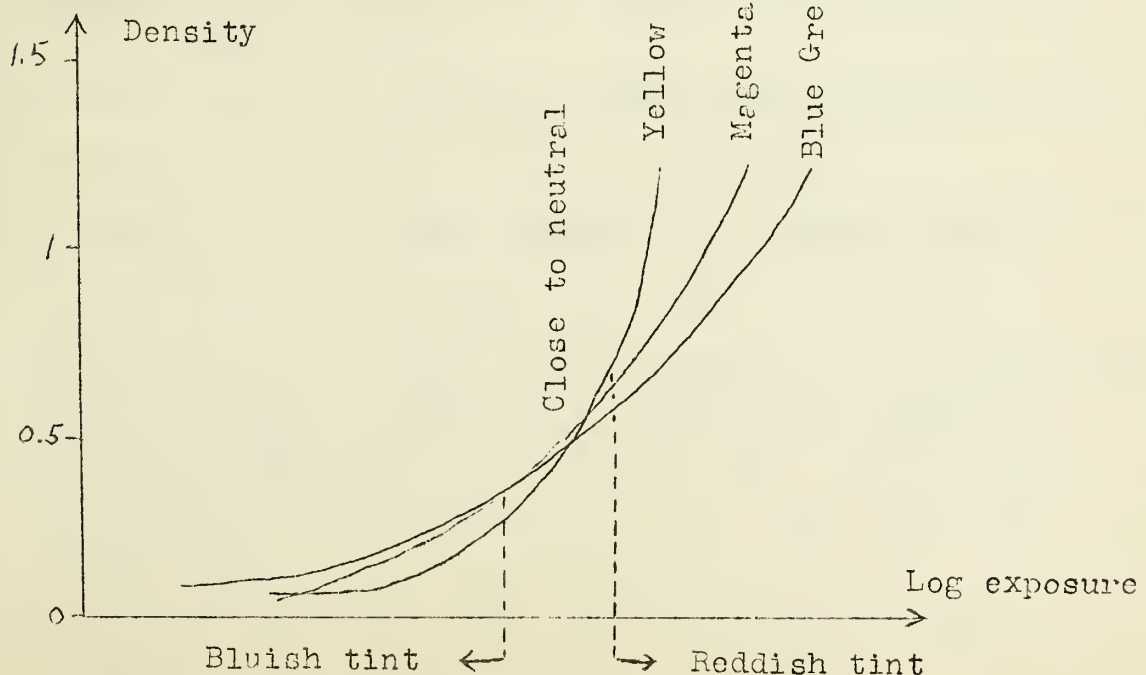
$W - R - G = B$
 $W - R - B = G$
 $W - G - B = R$
 $W - R - G - B = S$



Mixture of Colored Lights

Absorption out of white light

MATERIAL WITH THREE COLOR DENSITY CURVES, INCLINED WITH RESPECT TO EACH OTHER



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THE NATURE OF SODIUM METAPHOSPHATE GLASSES

R. Keith Osterheld

November 2, 1948

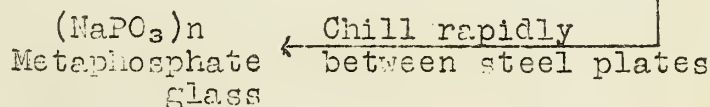
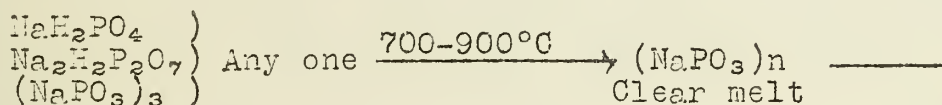
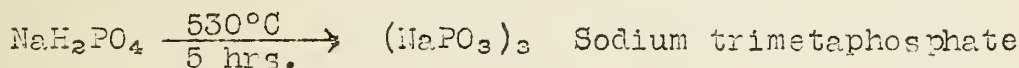
Introduction

The polymers of organic chemistry are well known and well characterized. Inorganic high polymers, on the other hand, often are well defined only in the solid state, generally undergoing decomposition when dissolved. Among those which exist both as solids and in solution are the "metaphosphate glasses." The discovery that organic polybasic acids (such as the "Trilons") had the power to complex calcium ions and thus soften water, lead to intensive investigation of the field of condensed sodium phosphates, the anions of which may be considered as condensation polymers of the PO_4^{3-} tetrahedron.

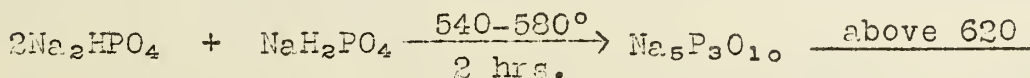
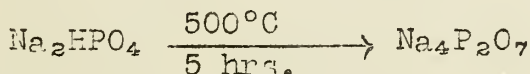
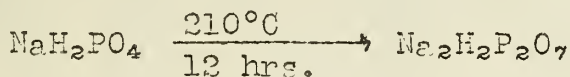
The linear polymers of this unit may be formulated as $\text{NaO}(\text{NaPO}_3)_n\text{Na}$. Only those polyphosphates in which $n=1, 2$, or 3 have been characterized as definite chemical individuals. Chains for which n has a higher value than 5 exist but probably only in mixtures. They undergo hydrolysis (or hydration) and tend to depolymerize to the shorter chains - ultimately to orthophosphate. The true metaphosphates may be formulated as $(\text{NaPO}_3)_n$. These must either be cyclic or possess a chain structure of extremely high molecular weight, in which case the polymetaphosphates become indistinguishable analytically from the polyphosphates. That is, $(\text{NaPO}_3)_n \sim \text{NaO}(\text{NaPO}_3)_n\text{Na}$.

Preparation of Sodium Metaphosphates

The molecularly dehydrated sodium phosphates may all be prepared by thermal means from mixtures of orthophosphates having the proper sodium to phosphorus ratios. The metaphosphates, then, are prepared by proper heat treatment of sodium phosphates having a Na:P ratio of 1:1.



For comparison, typical methods for the preparation of the linear phosphates are represented by the following equations:



Polyphosphate glass ←

Determination of Average Molecular Weight

It is proposed to limit the present discussion to the material known variously as "glassy metaphosphate," polymetaphosphate, "hexametaphosphate," Calgon, and Graham's salt. As a matter of historical interest, it was first reported by Graham (2) in 1834 and the name "hexametaphosphate" applied to it by Fleitmann (1) in 1849. The evidence in support of this name is extremely poor; in view of the work reported by van Wazer, such a designation has no justification.

Much of the early work with the metaphosphate glass was based on the assumption that this substance is a definite compound; consequently, many attempts were made to assign a formula to the material.

Jawein and Tillot (3), in 1889, determined the freezing point lowerings for approximately ten per cent solutions of Graham's salt in water and arrived at apparent molecular weight values of 389 and 407. Results of conductivity measurements led Pascal and Rechid (6), in 1932, to support the hexameric formula; they suggested, however, that the formula should be written: $\text{Na}_2(\text{Na}_4\text{P}_6\text{O}_{12})$. They obtained an apparent molecular weight value of 255 from cryoscopic measurements in water.

The question of differentiation of the degree of ionization of the "6" cations has been raised by others. A number of workers have prepared the polymetaphosphoric acid through the use of ion exchange resins or by decomposing lead "hexametaphosphate" with hydrogen sulfide. Salih (9) came to the conclusion that four of the hydrogens ionized freely while two were only slightly ionized. On the other hand, Treadwell and Leutwyler (11,12) and Rudy and Schloesser (8) reported that a single strong inflection is obtained in the titration of hexametaphosphoric acid. This agrees with the generalization that there is one strong hydrogen ion for each phosphorus atom in all phosphorus acids.

The molecular weight of glasses prepared at 650° has been determined through sedimentation studies with an ultracentrifuge (5). Results of these measurements lead to the conclusion that particles with average molecular weights of 12,000 to 13,000, corresponding to about 125 NaPO_3 units, are present in such solutions.

Other workers have recognized recently that the character of a metaphosphate glass is dependent on the conditions of preparation. Karbe and Jander (4) prepared the glassy material by fusing monosodium phosphate at various temperatures and then quenching the melt in carbon tetrachloride. Anionic weights of the products were obtained from determinations of dialysis coefficients in aqueous solution. Their results show a steady rise in molecular weight as the fusion temperature is increased from 650° (M.W. = 4850) to 1150° (M.W. = 9570). When the fusions were carried out at still higher temperatures, the molecular weight decreased, dropping to 3620 for fusion at 1250°.

Samuelson (10) carried out a similar study, using the technique of "end-group titration" to determine average molecular weights. His results ranged from 10,800 for fusion at 650° to 17,200 for fusion at 950°.

A rather complete study of the average molecular weights of glasses prepared from either monosodium phosphate or sodium trimetaphosphate under a variety of conditions was carried out by Weinberg (13), the molecular weights being obtained through end-

group analysis. Glasses prepared from the trimetaphosphate were found to have higher molecular weights than those prepared from the monosodium phosphate. Although only general trends could be established, the molecular weights were found to increase with rise in temperature and with time of heating.

Fractionation of Glass

Van Wazer (12) has carried out the most recent study and has fractionated solutions of the polymeric phosphate glasses with an Na:P ratio ≥ 1 , determining the average molecular weight of each fraction by terminal group analysis. A two per cent aqueous solution of the glass was fractionated by adding successive portions of acetone and separating the viscous liquid phase by centrifugation.

Results showed that Graham's salt, the so-called hexameta-phosphate, is not unique and that it differs only in degree of polymerization from glasses with higher Na:P ratios. As the ratio Na:P is increased from 1 to 1.67, the average chain length decreases. Increase in Na_2O content acts to terminate the chains by providing more terminal groups. Actually, this amounts to a depolymerization by base (oxide ion) in the fused state.

From a Graham's salt having an average chain length of 193 PO_3^- units (average molecular weight = 19,700), eight fractions were obtained, ranging in average chain length from 30 to 550 PO_3^- units (3060 to 56,100 in molecular weight). Van Wazer describes the metaphosphate glasses whose composition lies in the range for Na:P ≥ 1 as consisting of long chains with very little branching or cross linking.

Conclusion

The work of van Wazer gives the best picture of the nature of metaphosphate glasses. To a certain extent, the character of the material may be expressed in terms of its overall average molecular weight. In this case, however, it must be remembered that the average value does not reveal the extreme range of chain lengths and molecular weights.

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Color of Iodine Solutions

M. R. Hatfield

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I. Classification As To Color

Solutions of iodine may be roughly classed with respect to color in two groups, violet and brown. There are, however, intermediate tints ranging from violet-red to reddish brown, the color depending upon the nature of the solvent. This change of color with solvent has been of sufficient interest to chemists to make it the subject of a good many investigations.

According to A. Lachmann (1), iodine dissolved in pure solvents yields only violet or brown colored solutions. The intermediate tints are presumably due to impurities. Iodine gives a violet solution with chloroform; the progressive addition of alcohol causes the color to change from violet, to reddish-violet, to red, and finally to brown. In general, violet solutions are furnished by hydrocarbons, halogen compounds (except iodides), nitro compounds and carbon disulfide, while brown solutions are furnished by iodides, alcohols, ethers, ketones, acids, esters, nitriles, and certain sulfur compounds.

There is a general tendency for brown solutions to become violet when heated, and violet solutions to become brown when cooled (1)(2). For example, the violet solution in paraffin oil becomes brown at -90°C , and the brown solution in the fatty esters becomes violet at 80°C . On the other hand, the solution of iodine in ethyl ether remains brown up to critical temperature of the solvent.

II. Physical Properties

Even though iodine exists almost entirely in the diatomic state in all solutions (3)(4), the physical properties of the brown solutions are markedly different from those of violet solutions.

Solubility. In general, iodine is much more soluble in solvents giving brown solutions than in those giving a violet color. Hildebrand and his co-workers (5) have represented the solubility of iodine graphically by plotting the logarithm of the mole fraction of iodine in solution against the reciprocal of the temperature for various solvents. Violet solutions quite evidently form a family of curves whose position is determined by simpler factors than those operating with the brown solutions. The fact that solubility curves for the brown solutions do not fall in this family indicates that new molecular species are formed in such solutions. There appear to be no definite solubility trends for iodine in solvents giving brown colored solutions. Behavior in various solvents of this type can not be correlated with each other.

Distribution Coefficient. The distribution coefficient of iodine between two solvents which form violet solutions; or between two solvents which form brown solutions is relatively independent of temperature and concentration (6). The coefficient for two solvents, one of which forms a brown solution and the other a violet solution, is markedly

influenced by changes in temperature and concentration.

If the distribution coefficient of iodine between a "brown solution" solvent and a "violet solution" solvent is plotted against temperature, the graph reveals the fact that the successive differences in the values of the distribution coefficients tend to become smaller as the temperature increases. This is not surprising in view of the fact that brown solutions, upon heating, tend to change to a violet color.

Heat of Solution. The heats of solution of iodine in solvents which result in brown solutions are much greater than those for violet solutions (2).

Spectrophotometric Studies. The absorption spectrum of a violet solution of iodine is not very different from that of iodine vapor, although one is a band and the other a line spectrum. Violet solutions absorb heavily in the longer wave length portion of the visible spectrum, transmitting, beyond 12000 Å, both violet and all infra red light. On the other hand, brown solutions absorb heavily in the violet region of the spectrum (shorter wave length) and transmit at the red end. As might be expected, the spectrum of brown solutions shifts in absorption maximum toward the region of maximum absorption for violet solutions as the temperature is raised (7)(8).

III. The Nature of Iodine in Brown Solutions

Early investigators (10)(11) attempted to explain the peculiarities in the optical properties of iodine solutions by assuming a polymerization of the solute iodine which in the violet solutions contain I_2 molecules and in the brown solutions I_{n+2} molecules. Under any particular set of conditions, there is a state of equilibrium $I_{n+2} \rightleftharpoons nI_2$, which determines the color of the solution. Loeb(12) assumed that the iodine in the brown solution is present as I_4 molecules and in the violet solution as I_2 molecules. He explained the change from brown to violet with a rise of temperature by assuming that the equilibrium $I_4 \rightleftharpoons 2I_2$ is displaced in favor of the I_2 molecules.

Precise molecular weight determinations by Beckmann (3)(4) have proved that iodine is present in the diatomic state in all solvents investigated. In view of this fact, Beckmann suggested that there might be a partial combination of iodine with the solvent, S, to form a compound, say SI_2 . Under any particular set of conditions there is a balanced reaction: $SI_2 \rightleftharpoons S + I_2$. With violet solutions the amount of combination is very much less than with brown solutions and the spectra resemble that of iodine vapor.

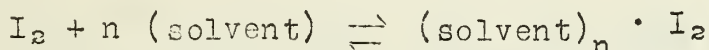
In fact, most investigators now account for the marked dissimilarities in properties between the brown and violet solutions by assuming that the brown solutions contain iodine chemically bound to the solvent, in equilibrium with free iodine. This assumption seems to be altogether reasonable in view of the fact that each of these "brown solution" solvents contains an element capable of acting as a donor in the formation of coordinate covalent bonds.

Iodine solutions in benzene have been sufficiently anomalous to warrant special attention. These solutions have

been reported by some as brown and by others as violet. The color of iodine-benzene solutions, even with very carefully purified benzene is not a pure violet, but rather violet-red, which changes to violet when the solution is heated. Several investigators infer the existence of a benzene-iodine complex, which might explain the peculiarity in color. Recently, Hildebrand and Benesi (9) have reported another absorption maximum for the violet-red iodine benzene solutions. This new absorption does not appear in solutions of iodine in hexane and carbon tetrachloride which are pure violet. This evidence, along with other evidence reported by them, points to the presence of an iodine-benzene complex consisting of one molecule of benzene and one of iodine. Their work is not yet completed but is being continued and will be submitted for publication soon.

Perhaps the most conclusive evidence of the existence of solvated iodine in brown solutions is the deviation from the theoretical calculation of the lowering of the freezing point of solutions upon addition of iodine. Hildebrand and Glascock (15) carried out freezing point studies on iodine solutions and showed that addition of a "brown solution" solvent to a violet solution changed the freezing point of the solution. In those cases in which the lowering is less than that calculated for the iodine on the basis of the dilute solution law, Hildebrand and Glascock conclude that there must be at least partial combination of iodine with the second solvent.

The same investigators studied the equilibrium for the reaction

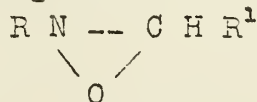


for various "brown solution" solvents in several media ordinarily giving violet solutions. Assuming $n = 1$, they obtained good concordance in the value of the equilibrium constants calculated from the equation

$$K = \frac{C}{C_b \times C_i}$$

where C_b = concentration of "brown solution" solvent
 C_i = concentration of iodine
 C = concentration of complex

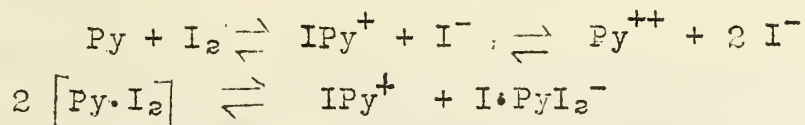
Molecular addition compounds of iodine with $(C_6H_5CH_2)_2S$; $(CH_3)_2S$; $(C_6H_5)_3CS$; C_6H_5S ; C_5H_5N ; C_9H_7N , and various substances of the general formula



have been prepared and in each case the compound adding to the iodine contains an atom which can act as a electron pair donor.

The exact nature of the bond between the iodine and the solvent molecule is still a mystery. Audrieth and Birr (14) have studied the electrical conductivity of solutions of iodine in pyridine, which increases with time. They found that in very dilute solutions, a constant value is very quickly attained. An extremely high molecular conductance at infinite dilution was also noted. Results were explained

by suggesting a gradual conversion of the initially formed non-conducting addition compound into a ternary salt, in accordance with the following mechanism:



Fairbrother (15) has recently submitted additional evidence of such amphoteric behavior of iodine in brown solutions. His results indicate that the formation of a red or brown solution is accompanied by polarization of the iodine molecule. Suppose that the proximity of an electron-donor stabilizes one of the possible ionic structures, $\text{I}^- - \text{I}^+$ and $\text{I}^+ - \text{I}^-$, of an iodine molecule. Then a partial ionization of the iodine takes place; the position end of the molecule being stabilized by coordination with a molecule of solvent.

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LOWER VALENCE COMPOUNDS OF ALUMINUM

R. Peavler

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Introduction:

Lower valence aluminum compounds have been known for only a short time. A series of aluminum (I) compounds has been identified, and there is some evidence for the existence of an aluminum (II) oxide. The existence of these compounds is not expected, since the higher elements of the group, gallium, indium, and thallium, have been known for some time to show the +1 and +2 states. In view of the relative instability of the lower states of gallium and indium, an even greater lack of stability for the corresponding aluminum compounds is to be expected.

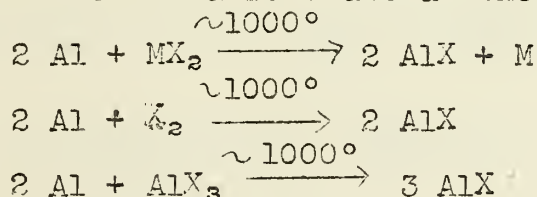
Aluminum (II) Compounds

In this series, some evidence has been found for the oxide AlO , but this evidence is far from conclusive. (1,2) Phase-diagram studies of the system $Al-Al_2O_3$ show a melting-point maximum at a composition corresponding to Al_3O_9 or approximately AlO . As in the case of gallium, aluminum II compounds could reasonably be expected to be unstable with respect to those of either the +1 or +3 state (3).

Aluminum (I) Compounds

Aluminum (I) compounds which have been studied include the halides, the sulfide, selenide and telluride (4,5,6). Their most evident characteristic is that they are stable only in the gaseous state and on condensation dissociate into aluminum metal and the aluminum (III) compound. Their boiling points are lower than the boiling points of the aluminum II compounds.

These compounds are formed at high temperatures, and appear to be the more stable state at those temperatures,



At high temperatures an equilibrium mixture exists:



This equilibrium is shifted to the right with increasing temperature. Aluminum (I) compounds are present in negligible amount at temperatures less than about 700° , but the amount increases rapidly with increasing temperature, and around 1000° the aluminum (I) compound is believed to make up the greater part of the equilibrium mixture.

The lack of stability of these compounds makes any study of their properties very difficult. Proof of their existence was obtained by distilling off the compounds in gaseous form, then condensing and determining the ratios of

aluminum to Al(II) compound in the condensate (sublimate). In the case of the fluoride, sulfide and selenide, analysis showed very close correspondence with the proportions which would be present in AlF , Al_2S and Al_2Se . At the temperatures used, neither aluminum nor the trifluoride, trisulfide or triselenide is volatile in substantial quantity, so all the sublimate must have come from the aluminum (I) compounds. Proof of the telluride and other halides is complicated by the fact that the aluminum (III) compounds are appreciably volatile.

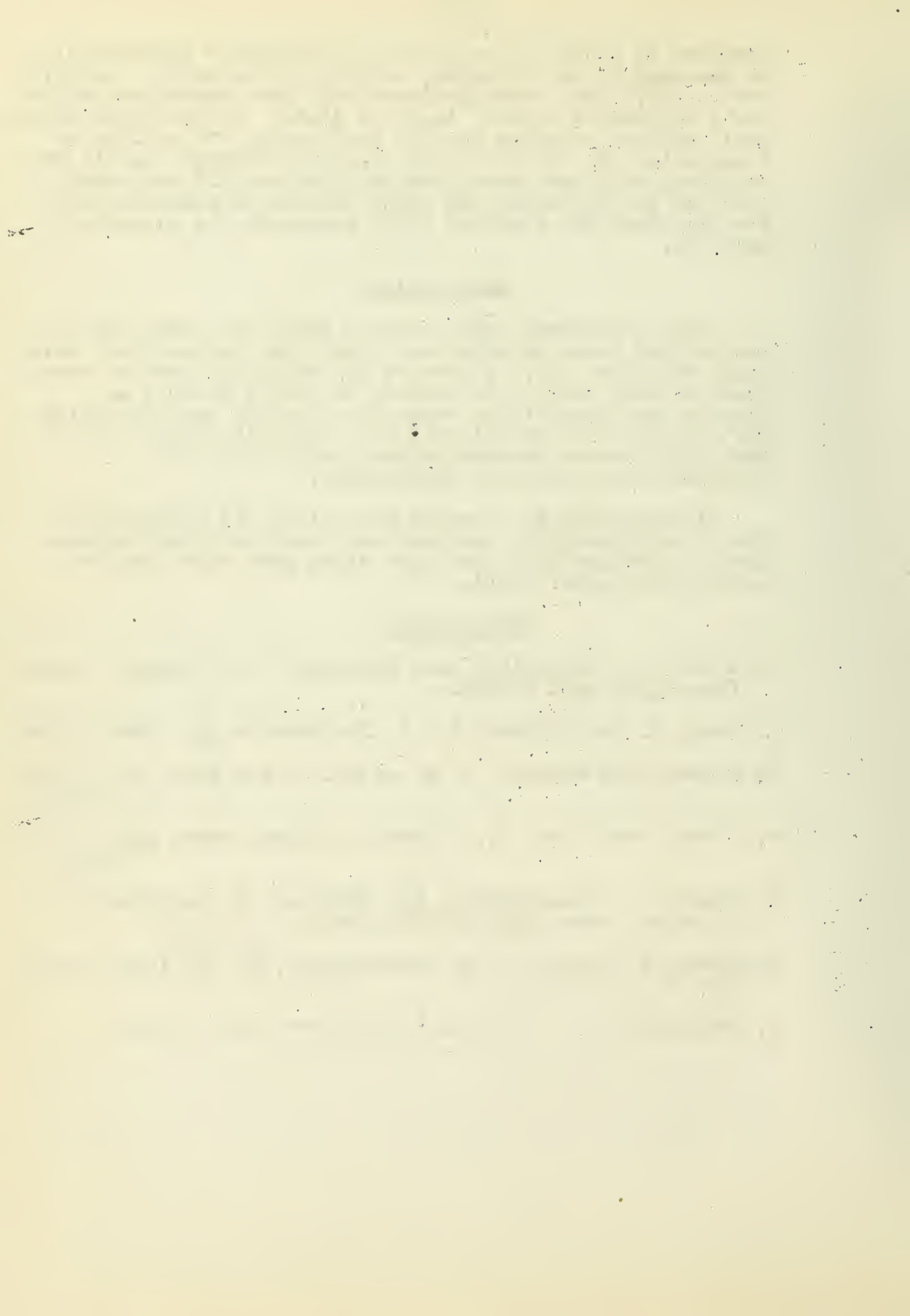
Application

These compounds have not been known for long, but one application seems to have been found even before their existence was known (7). A process for refining aluminum developed several years ago involved heating a mixture of aluminum and cryolite or magnesium fluoride and recovering the aluminum from the distillate. There is little doubt that this process depends on the distillation of aluminum as the volatile subfluoride.

Distillation of aluminum from alloys has been accomplished experimentally and has been found to effect separation of aluminum in a very pure state from such elements as iron and copper (5,6).

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COMPOSITIONS OF STRONG PHOSPHORIC ACIDS

Jennie C. I. Liu

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The history of the commercial production of phosphoric acids reveals continued effort to secure acids of great P_2O_5 content. It has been known that the acids, ranging in composition between $P_2O_5 \cdot 3H_2O$ and $P_2O_5 \cdot H_2O$ are mixtures. Attempts have been made to determine the various acids present in the mixture.

Preparation

Strong phosphoric acids are prepared (a) by dehydration of commercial 85% orthophosphoric acid by heating and (b) reaction of P_2O_5 with 85% orthophosphoric acid. Combination of these two may also yield a series of viscous products commonly called the "polyphosphoric acids". Such products are best characterized by specifying their P_2O_5 content. (1)

Analysis

Fiske and Subborow (2) determined the orthophosphoric acid content by a colorimetric molybdenum blue procedure. Bell (1) also determined the pyro- and triphosphoric acid contents. Pyrophosphoric acid was precipitated and weighed as zinc pyrophosphate and the triphosphoric acid was calculated from a modified Britske-Dragunor titration (16,3) after correcting for the pyrophosphate. The highly polymerized metaphosphoric acid usually referred to as "hexametaphosphoric" was determined by precipitating as barium hexametaphosphate in an acid solution and subsequent hydrolysis to orthophosphate (4). An unidentified acid which was found to be present in some preparations is believed to be a low polymer metaphosphoric acid, although no means of identifying it has yet been found. The quantity shown was determined by difference.

Composition

Results of the analysis of several liquid phosphoric acid mixtures varying from 72.2% to 88.9% P_2O_5 were obtained by Bell (1).

It is found that a product containing 72.2% P_2O_5 consists almost entirely of orthophosphoric acid. As the phosphorous content increases, the orthophosphate content decreases. Even when the product contains 88.9% P_2O_5 , a small amount of orthophosphoric acid is present.

A small amount of pyrophosphoric acid is present in a product containing 72.2% P_2O_5 . This increases to a maximum concentration between 77 and 79% P_2O_5 , where approximately 45% of pyrophosphoric acid is present in the mixture, then decreases until at slightly above 85% P_2O_5 no pyrophosphoric acid is found.

Triphosphoric acid does not reach its maximum concentration until P_2O_5 content is 83 to 85%, at which time 55% of the mixture consists of triphosphoric acid. It decreases somewhat thereafter but an appreciable quantity is still present in a strong phosphoric acid containing 88.9% P_2O_5 .

"Hexametaphosphoric" acid appears above 82% P_2O_5 and reaches its maximum concentration at the highest P_2O_5 concentration, 88.9%.

An unidentified acid is supposed to be a lower polymer of metaphosphoric acid. All attempts to identify this acid have been unsuccessful. Its barium salt was found to be insoluble above pH 10. Since the barium salt of trimetaphosphoric acid is soluble at pH 10, the unidentified acid must be some other meta-acid. It also does not convert to triphosphate when boiled with an excess sodium hydroxide as does trimetaphosphate. The amount of sodium

hydroxide neutralized checks very well when the unknown is calculated as a metaphosphoric acid. This acid appears in the mixture with a P_2O_5 content of 79%, reaches its maximum concentration around 83%, and then decreases to zero at 88.9%.

Identification

The P_2O_5 equivalents of the acid found by analysis were calculated for each of the mixtures and this calculated P_2O_5 was compared to the total found by analysis. The agreement between the two values is evidence that the compositions shown for the mixtures are correct.

Further proof of the composition was obtained by preparing the sodium salts from one of the acids. The crystallized sodium salts were identified by qualitative microchemical tests, refractive indices, and melting points. Crystals of trisodium orthophosphate, tetrasodium pyrophosphate and sodium triphosphate were obtained (5).

While qualitative tests may be used to identify the various acids, they can best be distinguished by the nature of the pH titration curves (3,7). Characteristic inflection points are obtained on titration of each acid with a base, corresponding to the existence of definite salts. It is found that exactly the same amount of base is needed to neutralize the strong acid function of each of the acids as is needed to neutralize the first hydrogen of the orthophosphoric acid on complete hydrolysis. All phosphoric acids, when titrated with base, shown an inflection point at pH 3.8-4.2, corresponding to neutralization of exactly one hydrogen per phosphorus atom. Additional hydrogen atoms above the H/P ratio of one are less readily dissociated and weaker, and show inflection points at higher pH values.

Van Wazer (7) titrated these acids with tetramethylammonium hydroxide rather than with sodium hydroxide, since "the presence of sodium ions distorts the titration curve due to complex formation".

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Richard H. Tennyson

November 16, 1948

I. Preliminary considerations

In general, compounds may be considered as belonging to one of two very broad classifications, namely: (1) compounds whose existence is explained on the basis of chemical bonds of various types, and (2) molecular compounds, formed when molecules interact through attraction of their permanent dipoles through dipole induction effects, or through dispersion forces. However, it has become apparent that there is a further type of molecular compound in which the component parts may be held together firmly even though none of the above listed forces appear to apply. This type of compound exists in the extreme case where a molecule of one component is completely enclosed by one or more molecules of another component in such a way that its escape is effectively prevented unless the forces which bind its surroundings together are overcome. Such compounds have been termed "clathrate compounds" from the latin "clathratus", signifying, "enclosed or protected by cross bars of a grating". (1)

II. Conditions for formation of such compounds may be summarized in outline form:

- A. Open crystal structure of the enclosing component, which necessitates:
 1. directed character of the links which hold the molecule and the crystal together, and which may be either
 - a. covalent bonds, or
 - b. hydrogen bonds
 2. sufficient linear extension of groups to form a cavity of suitable size
 3. a good degree of rigidity in the groups.
- B. Small size of the access holes to the cavity enclosed, which can be achieved in two ways:
 1. by proper disposition of rigid groups when packing occurs in the crystal
 2. by use of enclosing groups having a surface area sufficient to reduce the size of the access holes.
- C. Ready availability of the enclosed component at the time when closure of the cavity occurs.

III. Examples and properties of this type of compound.

The compounds are listed in decreasing degree of the certainty of their structure.

- A. Clathrate compounds of hydroquinone, approaching the general composition $(C_6H_6O_2)_3 \cdot M$, where M is known compounds is:

Increasing Length of Group		Shape of group	
HCl	(13, 5)	roughly spherical	increasing "c" dimension (5.47-5.81) in crystal
HBr	(12, 5)		
H ₂ S	(9, 5)		
C ₂ H ₂	(5)	linear	decreasing "a" dimension, (16.58-16.89) and increasing angle θ (5)
CH ₃ OH	(7, 5)		
HCOOH	(5)		
SO ₂	(10, 5, 7)	bent	
CO ₂	(5, 6)		
CH ₃ CN	(5)	linear	

MeOH-HCl (5)
 SO₂-HCl (5)
 HCOOH-CO (14,1)
 (C₆H₆O₂)₃.HCN (14)

CS₂ and C₂H₅OH are too large to enter the cavity, and H₂O is too small to be retained. (5)

- B. [Fe(CNCH₃)₆]Cl₂.3H₂O (1,2,3)
 C. Clathrate compounds of amines
 (p-NH₂C₆H₄OH)₁₀ . H₂SO₃ (17)
 (p-CH₃NHC₆H₄OH)₆ . H₂SO₃ (17)
 (p-NH₂C₆H₄NH₂)₉ . H₂SO₃ (17)
 D. Clathrate compounds of other phenols
 (s-CH₃C₆H₃(OH)₂)₂ . HBr (12)
 (s-C₆H₃(OH)₃)₂ . HBr (12)
 (C₆H₆O)₄ . SO₂ (15)
 (C₆H₆O)₅ . SO₂ (15)
 (C₆H₆O)₈ . CO₂ (11)
 (C₆H₆O₂)_x . CO₂ (x approaches 6) (6)

In general, the properties of these compounds are much the same as those of the parent or enclosing molecule. The crystal structures are roughly the same, and the melting points are the same with slight, if any, depression. They are stable when dry, and can be stored in the air or in vacuum without decomposition. The enclosed component escapes when the compound is dissolved or melted, and the component can then be recovered quantitatively.

IV. Summary of evidence supporting the proposed structure.

- A. The fact that clathrate compounds invariably melt either at the same temperature or only slightly below the temperature of the melting point of the enclosing substance indicates that the enclosed substance contributes little or no energy change other than the effects of slight distortion of cell dimensions in some cases.
 B. Hydrogen bonding is not involved in binding the molecule in the cavity.
 C. The distances between atoms of the enclosed and enclosing molecules are all van der Waal's equilibrium distances or are greater than these distances.
 D. The chemical properties of the compounds.

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The System: $\text{NH}_3 - \text{SO}_2 - \text{H}_2\text{O}$

Loh Wan-Chen

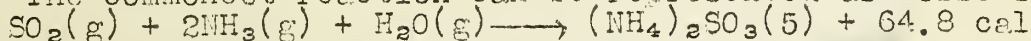
November 22, 1948

Both SO_2 and NH_3 are of industrial importance, both have secured attention as solvents in liquid form, and both substances are important heavy chemical commodities. The system $\text{NH}_3 - \text{SO}_2 - \text{H}_2\text{O}$ has been studied extensively and resembles in many respects the system $\text{NH}_3 - \text{CO}_2 - \text{H}_2\text{O}$.

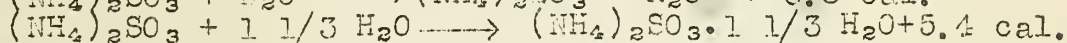
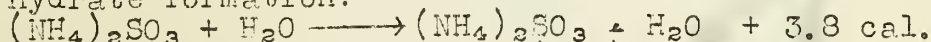
Reactions between Sulfurdioxide - Ammonia, and Water:

Because of the basic character of NH_3 and acidic character of SO_2 , they react readily in aqueous solution and form different salts under different conditions.

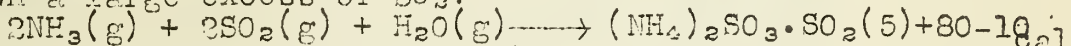
(1) The commonest reaction can be represented as follows:



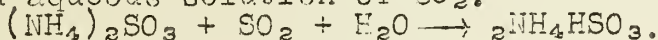
and hydrate formation:



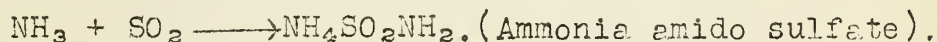
(2) With a large excess of SO_2 :



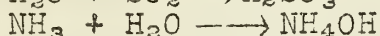
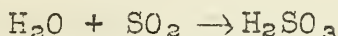
(3) NH_4HSO_3 is obtained when $(\text{NH}_4)_2\text{SO}_3$ reacts with saturated aqueous solution of SO_2 .



In addition, ammonia is said to react directly with SO_2 as follows:



In contact with water this product is converted into $(\text{NH}_4)_2\text{SO}_3$. Water dissolves both NH_3 and SO_2 in accordance with the simplified equations:



Gas - liquid equilibrium in the system $\text{NH}_3 - \text{SO}_2 - \text{H}_2\text{O}$

A complete examination of this system would have involved the determination of the composition and pressures of all phases, which contained all the components. The work was however restricted to the equilibrium conditions between solid and solution whose vapor pressure did not exceed one atmosphere, at ordinary temperature.

The partial pressures and solubility relationship on the binary systems $\text{NH}_3\text{-H}_2\text{O}$ and $\text{SO}_2 + \text{H}_2\text{O}$ can be represented by the Henry's law $P = Kc$, and vary with change of temperature.

For the ternary system $\text{NH}_3\text{-SO}_2\text{-H}_2\text{O}$. The partial vapor pressure have been studied by Terres and Hahn (2) and measured by H.F. Johnstone (4) at 35° , 50° , 70° and 90° for the purpose of correcting SO_2 in waste gas, over a long range of concentration of NH_3 and relative conc. of SO_2 in solutions of $\text{NH}_3\text{-sulfur-dioxide-water}$ system. The partial pressure may be expressed by the formulas:

$$P_{\text{SO}_2} = M \frac{(2S - C1^2)}{C - S} \quad \text{and} \quad P_{\text{NH}_3} = N \frac{C(C - S)}{2S - C}$$

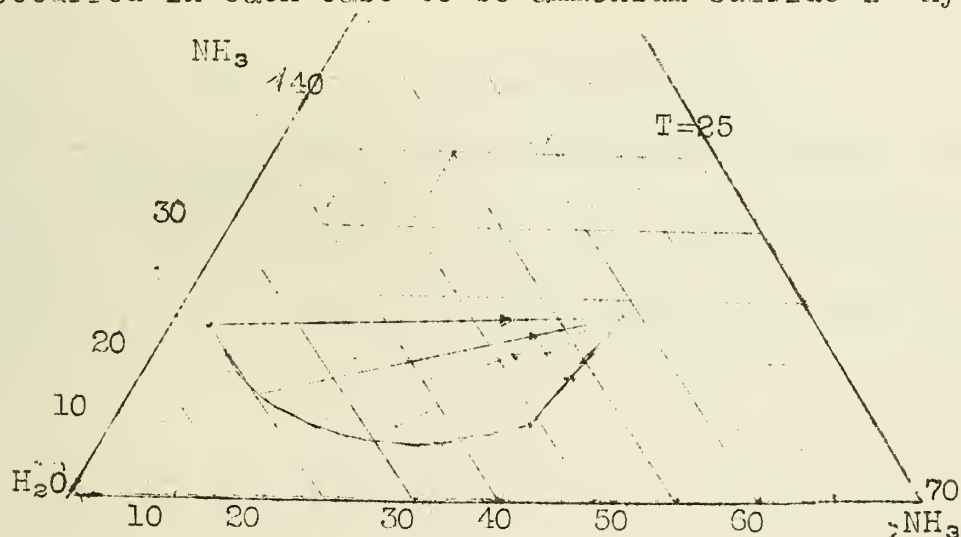
Where C is concentration of NH_3 in moles per 100 moles of water, and S is concentration of SO_2 , the coefficient can be represented as $\log M = 5.835 - 2369/T$ and $\log N = 13.680 - 4987/T$

The partial pressure of water follows Raoult's law.

Solid-liquid equilibrium in the system $\text{NH}_3\text{-SO}_2\text{-H}_2\text{O}$:

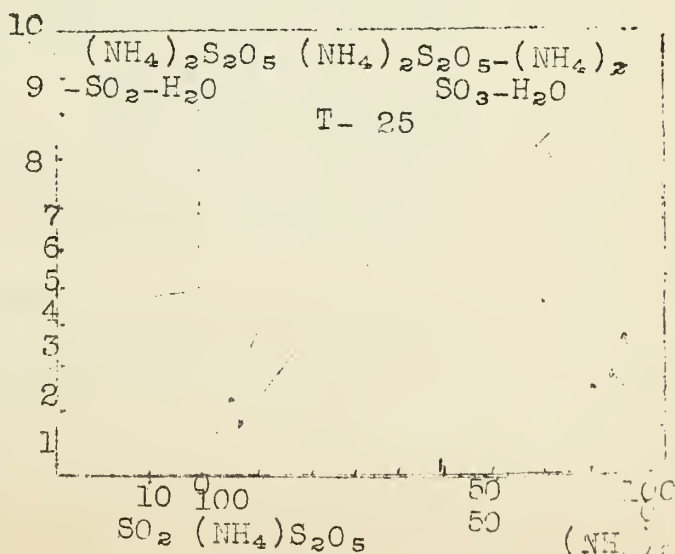
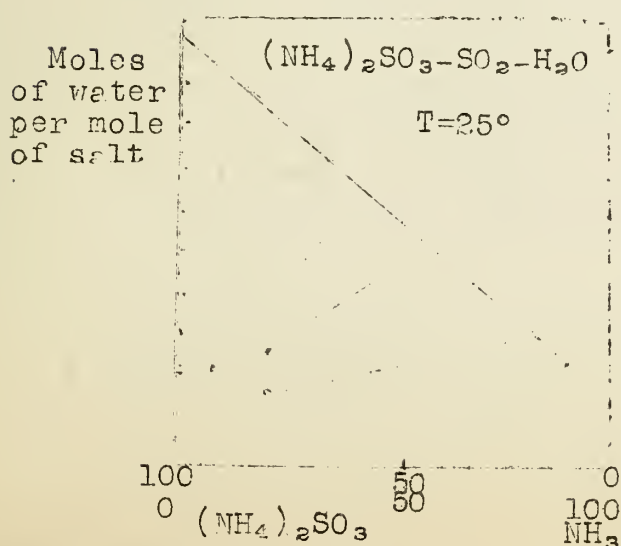
A partial study has been published by L. M. Hill (1). He mixed freshly distilled water, reagent ammonia solution, gaseous ammonia where required, and gaseous sulfur dioxide in different proportions; each mixture was placed in a container, the air displaced to avoid oxidation, and stirred thermostatically; seed crystals of $(\text{NH}_4)_2\text{SO}_4$ were then added. Equilibrium was established after about 17 hours. The solution and the moist solid were then analyzed.

The composition of the solutions and of the corresponding moist residue were plotted on tri-coordinate graph paper. The composition of the solid phase was determined graphically by plotting solution and moist solid composition. It was occurred in each case to be ammonium sulfide 1- hydrate.



The most extensive study of this system was published by Terres and Kahn. It was found that two different solid phases $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ and NH_4HSO_3 are in equilibrium with different proportion of the components. Over a certain concentration of sulfur dioxide, only NH_4HSO_3 is capable of existence. NH_4HSO_3 is shown to be more soluble than $(\text{NH}_4)_2\text{SO}_3$. A solid model was constructed to represent the equilibrium compositions in solution as a function of temperature.

The systems of $(\text{NH}_4)_2\text{SO}_3\text{-NH}_3\text{-H}_2\text{O}$; $(\text{NH}_4)_2\text{SO}_3\text{-(NH}_4)_2\text{S}_2\text{O}_5\text{-H}_2\text{O}$ and $(\text{NH}_4)_2\text{S}_2\text{O}_5\text{-SO}_2\text{-H}_2\text{O}$ were also studied by Fusco and Hiroshi (3); phase compositions and equilibrium were also determined by analysis of the solution and of moist solid. Results are represented on the following diagrams:



[illegible]

These figures show that $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ always constituted the solid phase, until 100 g. of solution contain 70 gm of $(\text{NH}_4)_2\text{S}_2\text{O}_5$ becomes the solid phase, no basic salt is formed even in concentrated ammonia solutions. The solubility of $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ decreased regularly with increasing content of NH_3 in the solution. The relationship can be represented by the equation

$$(\text{NH}_4)_2\text{SO}_3 = 39.45 - 1.346 \text{ CNH}_3$$

References:

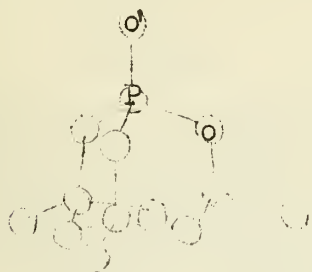
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THE GROUP FIVE OXIDES: THE CORRELATION OF
CRYSTAL STRUCTURE WITH CHEMICAL PROPERTIES

Claude R. Hudgens

November 23, 1948

In the gaseous state the P_4 tetrahedron may be identified in P_4O_6 and P_4O_{10} . The oxygen atoms are arranged along the edges and the corners of the tetrahedron as given in the figure and table¹.



	P_4O_6	P_4O_{10}
P--P	2.95A	2.84A
P--O	1.65	1.62
P--O'		1.39

There will be noticed a slight shrinkage of values in the transition from the lower to the higher oxide,

If the gaseous P_4O_{10} be condensed, the metastable form is obtained. This form is rhombohedral, space-group $R\bar{3}c$; with dimensions of the P_4O_{10} molecule the same as in the vapor state, and with $a = 7.43A$, $\alpha = 87^\circ$, density = 2.30, 4 molecules/unit cell². This is a body-centered form in which P_4O_{10} exists as discrete molecules. If this unstable crystal form is treated at elevated temperature, it changes over into the more stable orthorhombic form. Crystallographic description is:

Space-group: Fdd	8 P_2O_5 / unit cell
$a = 16.3 A$	
$b = 8.12$	P--P = 2.80 A.
$c = 5.25$	P--O = 1.65
density = 2.72	P --O' = 1.40

The crystal consists of an infinite lattice of PO_4 tetrahedra, each of which is bonded at the four corners with its neighbors. No molecules as such exist. A small warpage of the phosphorous valence angles occurs.

Vanadium forms a series of oxides ranging in composition from VO_2 to V_2O_5 , which change in crystal structure at certain points along the phase curves. VO has the NaCl structure, with $a = 4.10 A$, $V--O = 2.05A$.⁴ VO_2 has not been studied thoroughly, but is believed to have the rutile structure (SnO_2), tetragonal, $a = 4.54 A$, $c = 2.88$.⁵ V_2O_3 is rhombohedral, space-group $R\bar{3}c$, $a = 5.45 A$, $\alpha = 53^\circ 49'$, 2 mols./ unit cell, and is isomorphous with Fe_2O_3 , Ti_2O_3 , and Cr_2O_3 .⁶ With V_2O_5 there is a sudden return to a situation which is similar to that found in the case of P_2O_5 . Crystallographic description is:

Space-group: Pmn	2 mols./unit cell
$a = 11.48 A$	$V--O' = 1.57 A$.
$b = 4.36$	$V--O'' = 1.83$
$c = 3.55$	$V--O''' = 1.77$
	$V--O'''' = 1.75$

The arrangement has been shown to consist of chains of VO_4 tetrahedra which are closely laid parallel to each other so that sheets parallel to the $O10$ planes are formed. This may be demonstrated by the manner in which rods of V_2O_5 build up from colloidal suspensions⁸.

As_2O_3 and Sn_2O_3 (M_2O_3) are identical in configuration. The elementary R_4O_6 unit is the same as in P_4O_6 . These molecules take up positions at the points of the diamond

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lattice, $Fd3m$.¹⁰ Other data are:

	As_4O_6	Sb_4O_6	Reference
a	11.06 A.	11.14 A.	9
M--O'	1.80	2.0	9
M--O''		2.10	10
M--M	3.23		10
density	2.861	5.11	10

In the case of Sb_4O_6 , the shortest O--O distance from molecule to molecule is 2.86 A.¹⁰ There are eight M_4O_6 molecules per unit cell. The interatomic distances in As_4O_6 vapor have been found to be the same as those in the solid ¹¹.

Sb_2O_4 and Sb_2O_5 have identically the same crystal structure as Sb_2O_3 . In both, $a = 10.22$ A.¹²

CbO has been reported to be a defect lattice of the NaCl type, which contains three, instead of four, molecules. CbO_2 possesses the rutile structure, $a = 4.77$ A., $c = 2.92$ A.¹³

Bi_2O_3 occurs in a simple cubic, a tetragonal, and a monoclinic form. Information on the monoclinic form is incomplete. The simple cubic form is defined as $a = 5.525$ A., 2 mols./unit cell, in which B--O = 2.40 A., O--O = 2.76 A. The bismuth atoms are all equidistant from the oxygens. If the unit cell edge be defined as 11.06 A., the lattice becomes similar to that of Sb_4O_6 .¹⁴

Tetragonal Bi_2O_3 crystallizes in space-group $C4_2b$. Other crystallographic features are:

a = 10.93 A.	Bi--O	= 2.37 A.
c = 5.62	O'--O''	2.81
density = 9.18	O'--O'''	2.52 and 2.95
8 Bi_2O_3 /unit cell	O'--O''''	2.74

This cell is equivalent to four unit cells of the simple cubic form ¹⁴.

The activity of the metastable form of phosphorous pentoxide may be explained directly from its spatial configuration. It is noted that this is a molecular lattice, the molecules of which are held in the lattice by van der Waals' forces. These bonds are easily broken by any reagent, such as water. The atoms of the stable form of the pentoxide are bound by strong covalent bonds, therefore are correspondingly hard to break, thus, the more stable form reacts only very slowly with water.

VO and CbO bear a striking resemblance to FeO and CdO . All have the NaCl structure, all are defect lattices, and all are bound by approximately the same electrostatic forces. It could therefore be expected that many of their chemical properties would be shared in varying degrees.

VO_2 , and especially, CbO_2 may be expected to resemble SnO_2 chemically. V_2O_3 , due to totally unlike crystal structures, may be expected to have no resemblances to the corresponding phosphorous, arsenic, and antimony compounds, but would be expected to be very similar to ferric, chromic, and aluminum oxides. V_2O_5 should be somewhat less resistant to water than the stable form of P_2O_5 .

Arsenic and antimony oxides are packed in the densest possible molecular lattice, therefore would not be expected to have the reactivity of P_4O_6 . The lattices, however, are distinctly molecular, therefore, little resistance should be

apparent to strong bases.

Bi_2O_3 , due to its ionic character, is expected to be completely acid soluble. There should be no appreciable difference in reactivity between the tetragonal and cubic forms.

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R. W. Meikle

November 30, 1948

Crystallography:-- The science of crystallography has been developed to a remarkable degree from the study of geometrical forms of crystals alone. With regard to external shape there are two laws that hold. The first of these is called the Law of Constancy of Angles. Angles between corresponding faces of different specimens of any particular kind of crystal are always found to be the same. The second is known as the Law of Rational Intercepts. If axes of reference are chosen in a suitable manner, then each of the faces of the crystal will cut any one of the axes at distances from the origin which stand to each other as small whole numbers. A particular face of a crystal is located with reference to the axes by the Miller indices.

The unit cell is a parallelepiped and contains an integral number of chemical molecules. The crystal is made up of a large number of these unit cells fitted together in regular fashion. The corners (as well as the cell-centers and other corresponding points) of the unit cells will form a three-dimensional series of points which is called a space lattice. This lattice is considered as indefinite in extent. However, the unit cell is the smallest portion of the crystal lattice which exhibits all of the various kinds of symmetry possessed by the crystal. It is important to keep in mind that it is not possible for a single unit cell to exist by itself without subdividing atoms. The boundaries of the unit cell in general pass thru the centers of atoms and the unit cell is therefore an imaginary concept.

Crystals are grouped into six crystal systems based upon the geometry of the reference axes. For each system there will be one or more lattices or arrangements of the unit cell. In the simple arrangement each corner of the parallelepiped will be occupied (fig. I). In the body-centered arrangement there will be in addition a point at the center of each parallelepiped (fig. II). A further variation in the arrangement is produced by points located in the center of some or all of the six faces (fig. III). The classification of the six systems is as follows:

1. Triclinic; faces of unit cell all parallelograms (no rectangles); one lattice with simple arrangement.
2. Monoclinic; unit cell a right prism; four faces rectangles, other two are not; two lattices: simple and base-centered.
3. Orthorhombic; a right prism, faces all rectangles; four lattices; simple, base-centered, face-centered and body-centered.
4. Tetragonal; a right prism; two faces squares, other four rectangles; two lattices, simple and body-centered.
5. Cubic; all faces squares; three lattices; simple, face-centered, and body-centered.
6. Hexagonal; a right prism; four faces rectangles; two faces rhombuses with angles 60° and 120° .

The chemist is not so much interested in the geometry of the lattice as in the relations of the atoms to each other and to the molecule. We may recognize three types of crystals according to the nature of the binding forces. The simplest type may be termed the atomic type, where each atom is connected to the adjacent atoms by valence forces. A second type is the ionic crystal. The forces holding this type "together" are primarily electrostatic and there is no definite valence number associated with an ion. The third type of crystal may be called the molecular type. It is made up of molecules, and the forces between them are of the same weak character as van der Waals forces.

The generalizations of crystallography point to the conclusion that crystals are made up of ultimate units of definite geometrical shape which fit together in compact arrangements. This hypothesis is confirmed by x-ray investigation.

When x-rays are passed thru a crystal the discontinuous nature of the crystal is revealed in the diffraction pattern which is obtained. The spacing of the atoms or molecules in a crystal is of the same order of magnitude (10^{-8} cm.) as the wave length of x-rays and the crystal acts as a diffraction grating for x-rays. The atoms or groups of atoms in the crystal are in regular arrangement and from certain angles will appear to lie in layers. The primary analysis of a crystal consists of the determination of the distances between these layers. From these distances and the orientation of the various sets of lattices with respect to the crystal axes, the lattice can be constructed.

Description of the Structure:-- Cupric Chloride is one of the few halides of the commoner elements which has not previously been studied by the methods of x-ray crystallography. Its structure is of interest in view of the planar configuration of four bonds from a cupric atom, already established in a number of crystalline salts and co-ordination compounds. It is found that the structure of CuCl_2 , although closely related to that of PdCl_2 , differs from that structure (6).

The crystals are thin laths or needles, elongated along the "b" axis. There is perfect (001) cleavage, and moreover, the slightest pressure on a (001) plate causes it to split along its length into a bundle of fibres, looking much like asbestos. By reflected light the crystals appear brown, and they exhibit striking pleochroism. X-ray examination shows the crystals to be monoclinic as in figure (IV). It can be seen that there are two CuCl_2 per unit cell. The Cu and Cl atoms are joined together to form infinite chains in which each Cu is surrounded by 4 Cl in a plane and each Cl is attached to 2 Cu.

In figure (V) is shown the crystal structure of PdCl_2 (7).

From the similarity in the lengths of the "b" axes in CuCl_2 and PdCl_2 it may be concluded that the structure of a chain is very similar to that in PdCl_2 , or as shown in figure (VI) (6). The next nearest neighbors of a copper atom, other than the 4 planar Cl, are two more Cl in adjacent chains related by the face-centering. These complete the distorted octahedral arrangement of six bonds from each Cu atom. Taking account of this weak additional binding, the chains form sheets parallel to (001), though, of course, by far the strongest bonds are those within the individual chains, which run parallel to (010).

In PdCl_2 , on the other hand, there is no such suggestion of secondary bonds linking the chains laterally into layers, and the mode of packing of the infinite chains is much more like that of non-polar chain molecules such as long-chain hydrocarbons.

The Stereochemistry of the Cupric Atom:-- Perhaps the most interesting result of this study is the demonstration that the structure of the CuCl_2 is different from that of PdCl_2 . Both compounds form exactly the same type of infinite chain molecules, yet the chains are packed in different ways in the crystal of CuCl_2 and PdCl_2 . The environment of the Cu and Pd atoms with respect to Cl atoms in these crystals are shown in figures (VII) and (VIII), respectively. It has been shown that Cu^{++} has precisely this environment in a number of other crystalline salts (3). However, in cupric chloride dihydrate, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (4), the crystal structure varies somewhat from that for anhydrous CuCl_2 in

that two oxygen atoms replace two of the four planar chlorine atoms. It is argued that the displacement of two of the four possible chlorine atoms by two H_2O (to give $2H_2O$ and $2Cl$ as nearest neighbors instead of 4 Cl) is connected with the strong tendency of Cu^{II} to form bonds to oxygen--witness the numerous "basic" salts of copper (actually hydroxysalts).

It is supposed (6) that, when Cu^{II} forms four planar bonds, the 35 valency electrons are distributed among the available orbitals as follows:

2	8	2	6	8+2	2	4+1
				shared		

The odd electron occupies a 4p orbital. It seems possible that this electron may have some bonding power and might be responsible for two additional weak bonds perpendicular to the plane of the four strong dsp^2 bonds.

I

II

III

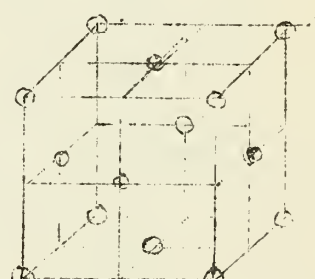
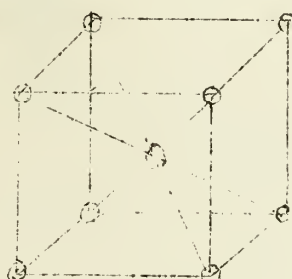
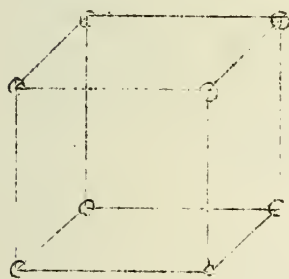
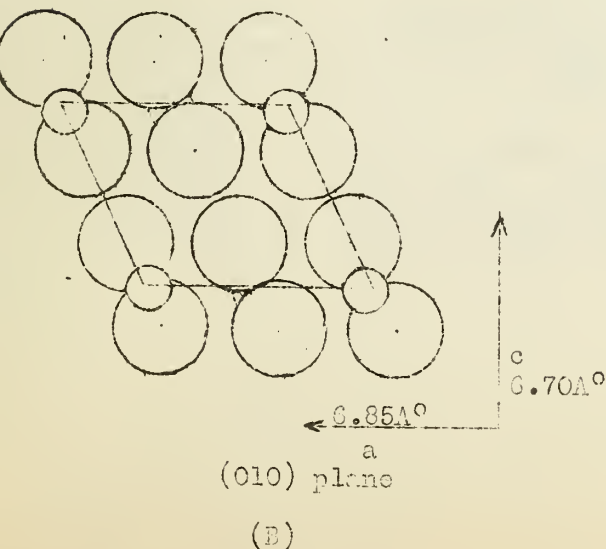
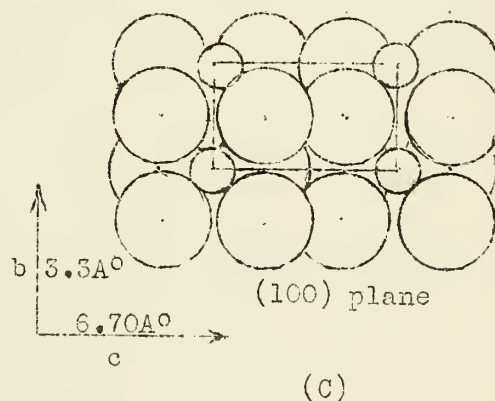
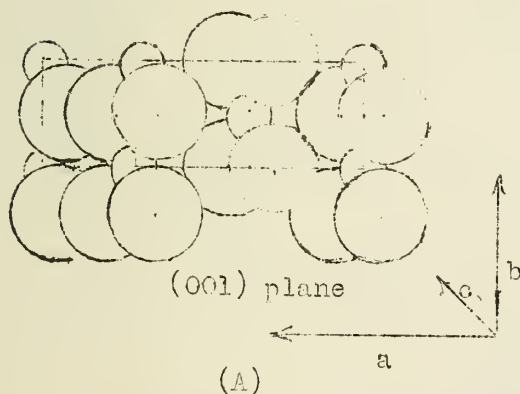


Fig. IV



Crystal Structure of Anhydrous $CuCl_2$ (unit cell)

Fig. V

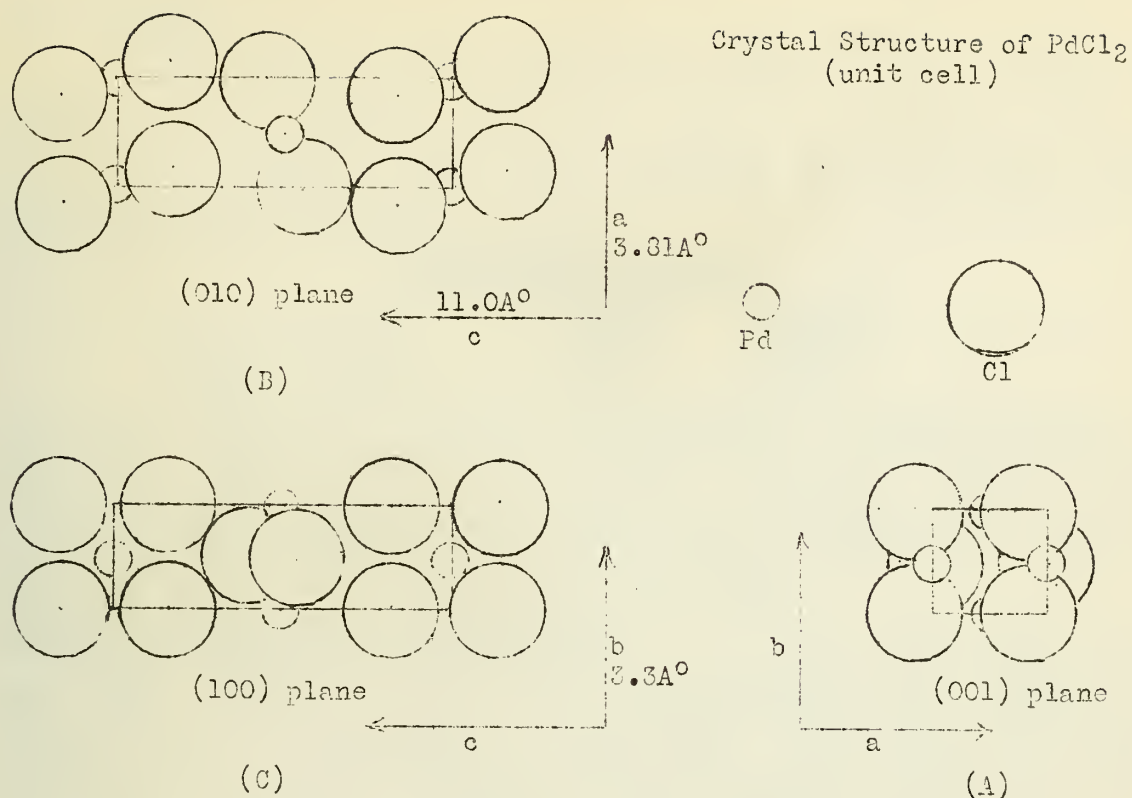


Fig. VI

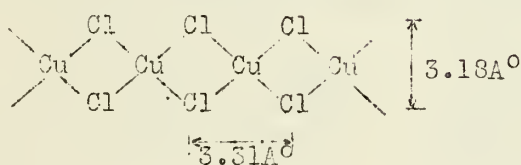


Fig. VII

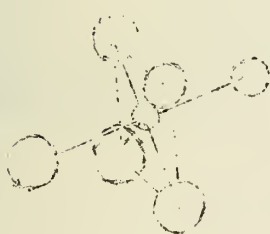


Fig. VIII



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THE SEPARATION OF HAFNIUM FROM ZIRCONIUM BY LIQUID - LIQUID EXTRACTION

W. H. McCurdy, Jr.

November 30, 1948

Introduction

Although interest in hafnium has been largely academic, certain of its properties, such as refractory nature, electron and light emissivity, low temperature coefficient of resistance, etc., have brought about increased commercial demand for this element in recent years. Thus far, the main drawbacks preventing the satisfaction of this demand have been the cost and difficulty of isolating hafnium free from zirconium.

Size Relationships

	Zirconium	Hafnium
Atomic Radius	1.60A°	1.59A°
Ionic Radius (+4)	0.80A°	0.86A°
Atomic Volume	14.06cc	13.43cc

The great similarity of size relationships (see above) and the resulting slight differences in properties are responsible for the separation difficulties encountered. In general, hafnium compounds are more ionic, slightly more basic, and slightly less readily hydrolyzed than those of zirconium. These differences are the basis of most of the separations attempted.

Summary of Methods of Separation

While zirconium and hafnium may be separated together from most other elements (e.g., the phenylarsonates (9), $(\text{NH}_4)_3 \text{MF}_7$ (7), MOCl_2 (7) or ion exchange (8), no single-step operation has been devised for the resolution of these two. Several of the more effective fractional methods are summarized in Table I.

Table I. Methods of Separation of Hafnium from Zirconium

Method	Compound	Process	Comment	Reference
Fractional	1. K_2MF_6	- Hf compd. 1.5 times more soluble	Several thousand	6,7
Crystallization	2. MOCl_2	- Hf compd. least soluble in 12N HCl	recrystallizations	6,7
	3. $\text{M}(\text{cit})_2$ or oxalate	- Hf compd. more soluble	regd. for 99% HfO_2	10
Fractional	1. $\text{H}_3(\text{PO}_4)_4$	- H_3PO_4 and MOSO_4 solns sprayed together. Hf compd. is more insoluble	7 ppt. give 93% HfO_2	11
Precipitation	2. $\text{M}(\text{SO}_4)_2$	- $\text{M}(\text{SO}_4)_2$ slowly hydrolyzed with triethyl phosphate. Hf ppts. first as $\text{M}(\text{HET}^+ \text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	6 ppt. give 95% HfO_2	12
	3. $\text{MFe}(\text{CN})_6$	- $\text{Na}_4\text{Fe}(\text{CN})_6$ added to a $\text{M}(\text{SO}_4)_2$ soln. containing oxalic acid. Hf ppts. first.	4 ppt. give 80% HfO_2	10
Fractional Distillation	1. MX_4 (X=Cl or Br) or $\text{MCl}_4 \cdot \text{PCl}_5$	HfBr ₄ - 595°K sublimes ZrBr ₄ - 630°K sublimes	Difficult to do experimentally	4

Numerous other methods are recorded in the literature, but all are more or less objectionable from the following standpoints:

1. Time consumption - especially filtration and washing operations
2. Step separation effect - usually small, requiring numerous steps
3. Yield and purity of hafnium - rarely above 95% HfO_2
4. Commercial applicability - operations too tedious and costly

W. Fischer and W. Chalybaeus recently published two papers describing an ether-water multiple extraction procedure employing the (Zr, Hf) thiocyanates and yielding a 99.6% HfO_2 product (1,2)

Liquid-Liquid Extraction

1. Discussion

The familiar distribution of a solute between two immiscible solvent results as a thermodynamic requirement for equilibrium. If the same molecular species exists in both solvents, then the distribution of solute between solvents A and B at a given temperature may be expressed by: $\frac{a_A}{a_B} = K$

where a = activity of solute

K = distribution coefficient

Although the (Zr, Hf) thiocyanate - ether - water system is exceedingly complex, the authors were able to follow the separation trends using this fundamental relationship. Data were collected to make the following distribution calculations possible.

(a) ϕ_E = degree of extraction (i.e. ϕ (Zr, Hf)O₂ extracted)

(b) ϕ_P = ϕ HfO₂ in ether layer (b) " ϕ_A = ϕ HfO₂ yield

(c) Observed Coefficients of Extraction

$$\alpha_{Zr} = \frac{C_{ZrO_2}(\text{Ether})}{C_{ZrO_2}(\text{Water})} \quad \alpha_{Hf} = \frac{CHfO_2(\text{Ether})}{CHfO_2(\text{Water})}$$

where

C = concentration

α = coefficient of extraction

(d) Separation Factor

$$B = \frac{\alpha_{HfO_2}}{\alpha_{ZrO_2}}$$

The extract samples were all ignited to the oxides and analyzed by X-ray comparison techniques. Thus, a measure of yield and purity of hafnium (IV) oxide was secured after each extraction

2. Effects on (Zr, Hf) Thiocyanate Distribution (Water - Ether)

Almost all of the effects described can be directly attributed to hydrolysis of the zirconium and hafnium compounds in solution. The coefficients of extraction were strongly affected by changing conditions whereas the separation factors appeared to be surprisingly constant with a given hafnium concentration.

(A) Solvent

Among the numerous alcohols, esters and ethers studied, diethyl ether was selected because of the favorable separation factor obtained by using this solvent. Since diethyl ether is a polar organic solvents, the solute extracted is possibly a non-ionized or slightly ionized complex (13).

(B) Anion Electrolyte

The character of the anion electrolyte has a marked effect on the magnitude of extraction and hydrolysis which occur during the distribution process.

1. Cl⁻ - enhances the extraction of zirconium by the ether layer
2. SO₄⁼ - lowers the ϕ extraction and yields slight zirconium enrichment of the ether layer
3. SCN⁻ - strongly favors the extraction of hafnium by ether
4. Ac⁻ - allows hydrolysis to predominate giving practically no extraction.

Note that the presence of thiocyanate reverses the normal order of the zirconium and hafnium extraction tendency. The authors suggest that the hafnium complex thiocyanate is more stable than the corresponding zirconium complex due to the ease of polarization of the linear thiocyanate ion. (4,5). Perhaps a better explanation would point to the greater rate of hydrolysis of the zirconium thiocyanate as compared to the rate for the hafnium compound. After a short time, the zirconium complex has hydrolyzed to a certain degree where it is no longer extractable while the situation has not been reached by the hafnium complex and therefore it is still capable of being extracted.

(C) Acidity

Addition of a strong acid was found to be necessary before any appreciable extraction took place. Sulfuric acid was chosen for this purpose. In the absence of this acid, the aqueous phase became turbid with hydrolysis products precipitated from solution

by the dissolved ether.

From the above three effects, the following extraction system was established.

<u>Aqueous Layer</u>	<u>Ether Layer</u>
(Zr, Hf) Sulfates + NH_4SCN + H_2SO_4	(Zr, Hf) Thiocyanates + HSCN

Further study of conditions made possible the perfection of this system.

(D) Concentrations

- | Material | Effect |
|---|---|
| 1. Increasing SO_4^{2-} concentration | = decreases the extraction coefficients (α_{Hf} and α_{Zr}) |
| 2. Increasing NH_4SCN concentration | = increases the extraction coefficients (α_{Hf} and α_{Zr}) |
| 3. Increasing ether volume | = increases the % E but decreases the extraction coefficients |

It is also important to note that both α_{Hf} and the separation factor (B) increase with increasing % HfO_2 in the sample. This somewhat unusual relationship exists because the solutions rich in hafnium are less inclined to hydrolyse than those rich in zirconium. The result is an increase in extractable material in the aqueous layer.

(E) Time and Temperature

The degree of hydrolysis will of course increase with increasing time and increasing temperature. The coefficients of extraction will undergo a corresponding decrease. The best separation as regards these effects was obtained at 10°C in a period less than 30 minutes. Since the distribution equilibrium is rapid, the zirconium hydrolysis fairly rapid, and the hafnium hydrolysis much slower, a very short mixing time was found to be most efficient.

3. Effects on (Zr, Hf) Thiocyanate Distribution (Ether-Water)

A brief but conclusive study was made of the extraction of the zirconium thiocyanate plus thiocyanic acid-ether layer with water layers containing various amounts of ammonium thiocyanate, ammonium sulfate, and sulfuric acid. The effects on Zr and Hf were observed to be approximately the same as for the previous work except that the materials were being extracted into the aqueous phase (zirconium more readily than hafnium).

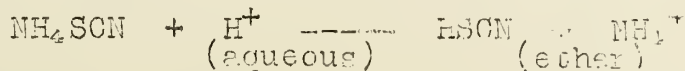
(A) Anion Electrolyte in Aqueous Phase

1. Increasing SO_4^{2-} concentration - favors extraction of solute into the aqueous layer
2. Increasing NH_4SCN concentration - favors retention of solute by the ether layer.

Results

Using the effects described above, Fischer and his co-workers devised an ingenious multiple-step process for the preparation of pure hafnium compounds. The optimum degree of extraction could not be employed since the purity of the hafnium (IV) oxide would be diminished. A compromise had to be made between yield and purity. The essential facts concerning the conditions employed are listed below:

(1) The aqueous layer containing the dissolved (Zr, Hf)(SO_4)₂ prepared from (0.5% HfO_2) + H_2SO_4 + 4-5 NH_4SCN was extracted ten times with later portions of diethyl ether 1.5 M in HSCN . Additional acid was required after each extraction to prevent undue hydrolysis since hydrogen ions are removed from the aqueous layer by the reaction:



By this first operation, the % HfO_2 was increased from 0.5% to 10% HfO_2 .

(2) This ether layer was next extracted with a series of aqueous layers (4 or 5 steps) containing decreasing ammonium thiocyanate concentrations (steps 1-5) and increasing ammonium sulfate

concentrations (steps 1-5). Most of the zirconium was extracted in the first two steps, leaving the last fractions considerably enriched in hafnium.

(3) These hafnium rich layers were worked up and extracted again with ether containing thiocyanic acid. The process thus consists merely in repeating operations No. 1 and No. 2.

In this manner, a product containing 99.6% hafnium(IV) oxide was obtained in 65% yield using an eight step extraction of 60% hafnium material. A fourteen step process was required to work the 0.5% hafnium samples to this point.

Analysis of Final Product

99.6% HfO_2 , 0.2% ZrO_2 , 0.1% Al_2O_3 , 0.05% Fe_2O_3 , 0.07% TiO_2

Summary

The separation of hafnium from zirconium by ether-water thiocyanate extraction depends upon three important factors:

1. Zirconium thiocyanate hydrolyses more rapidly than the hafnium compound. The hydrolysed products are not readily extracted by ether.

2. The distribution equilibrium for the system is rapid and thus is able to take utmost advantage of the differential hydrolysis rates of the (Zr, Hf)thiocyanates.

3. The stepwise enrichment improves as the % hafnium (IV) oxide in the sample increases. This simplifies the separation process.

Significant advantages of this method over present procedures may be noted. Each step is much easier and capable of being repeated more rapidly than with any precipitation method. The ultimate product contains a degree of purity difficult attainable by any other method. Lastly, the method offers a possible basis for a commercial continuous-flow extraction process.

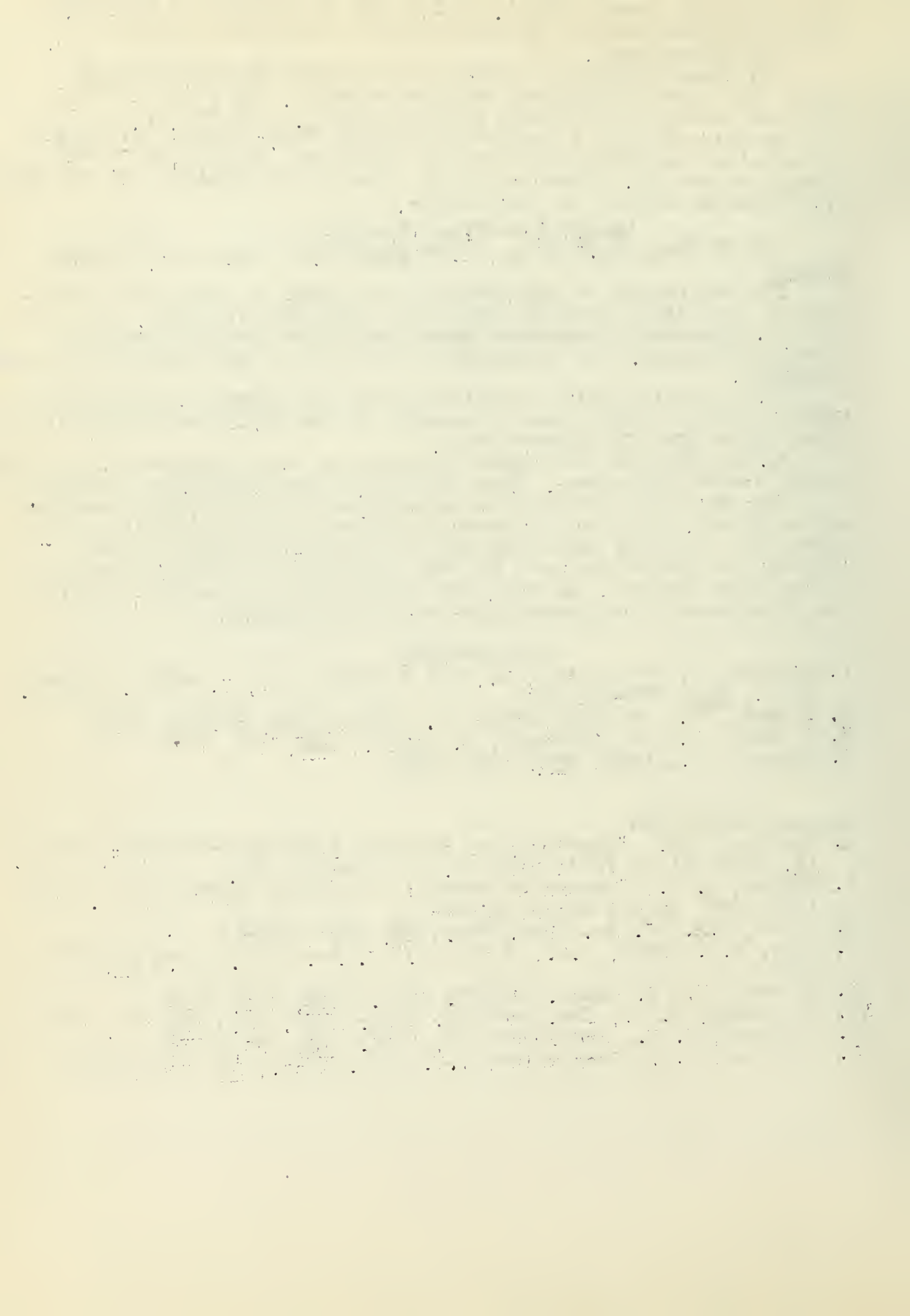
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THE CHEMISTRY AND STRUCTURE OF NITRYL CHLORIDE

Philip D. Caesar

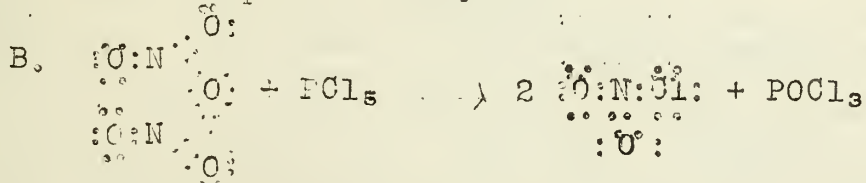
December 7, 1948

Nitryl chloride (NO_2Cl), also known as nitroxyl chloride, was first prepared in the pure state by Schumacher and Sprenger (3) in 1929, although its preparation was first described by Williamson (6) in 1854 and by eight or ten others in the interim. It is a colorless gas which decomposes into NO_2 and Cl_2 at temperatures above 120° (4). It boils at -15° and melts at -145° .

Preparation: Pure nitryl chloride is best prepared by either of the following methods, which are described in detail by Schmeisser (2). (The electronic configurations depicted here are not those recommended by him, however.)



This reaction was carried to completion in two stages in an all-glass apparatus. By condensing the reactants and products with liquid air before and after each step, it was found possible to keep the system free of extraneous gases. Excess ozone was removed by allowing the products to stand in a cold bath kept at -120° .

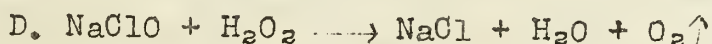
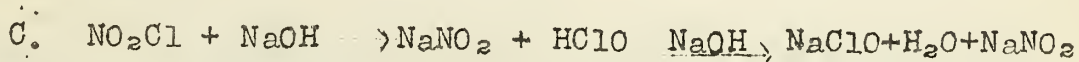


Pure N_2O_5 was prepared by the reaction of nitric acid with phosphorus pentoxide in the presence of ozone at a temperature of 50° . Phosphorus pentachloride was added to the N_2O_5 cooled in liquid air, and the reaction was then carried out carefully at -55° , in order to minimize the formation of NOCl , Cl_2 , etc. The bright yellow liquid product was evaporated at -98° under subatmospheric pressure and the vapors passed through a series of cold traps, the first of which was kept at -100° , the second at -117° , and the last two at liquid air temperatures. The pure colorless NO_2Cl was isolated in the trap kept at -127° .

The products obtained by each of these procedures were shown to be identical by vapor pressure-temperature measurements and by the similarity of their chemical reactions.

Chemical Reactions

I. Hydrolysis (2)



A carbon tetrachloride solution of NO_2Cl was treated with 10% NaOH , and a 3% solution of H_2O_2 then added in order to remove the hypochlorite in accordance with equation D. The reaction proceeds quantitatively in accordance with equation C, based on determination of the oxygen gas evolved and the chlorine content of the sample.

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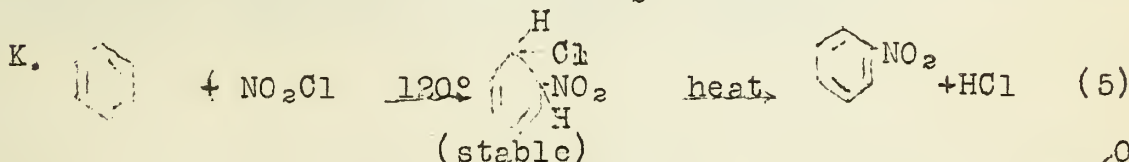
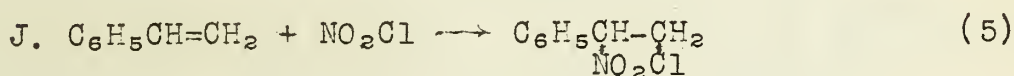
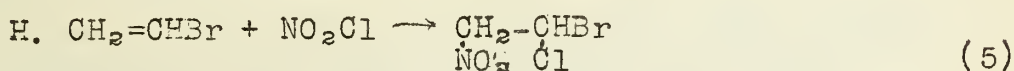
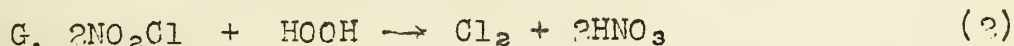
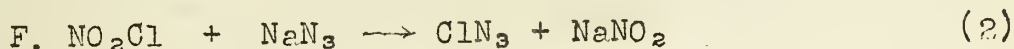
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II. Ammonolysis (2)

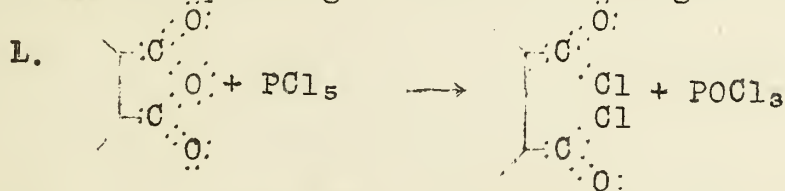


This reaction was carried out at -70° and the excess NH_3 removed at -96° under vacuum. At -40° a fraction distilled off which was identified by its "chemical properties and physical constants" as chloramine. The residue was found to be ammonium nitrite.

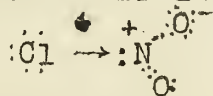
III. Miscellaneous



Structure Two structures for NO_2Cl have been proposed, $\text{O}=\text{N}^+-\text{O}^-\text{Cl}$ and $\text{O}=\text{N}-\text{O}-\text{Cl}$. The former (1) was tacitly assumed until Schmeisser (2) in a recent article objected to it on the grounds that the chlorine atom could not display the electropositive character shown in reactions C through G, if it were the chloride of nitric acid. He considered the "nitrosylhypochlorite" structure shown above to be the only one which would account satisfactorily for the electropositive chlorine. Several objections may be advanced to his line of reasoning: 1. The preparation of NO_2Cl according to reaction A would certainly suggest the oxidation of nitrogen from +3 to +5, whereas its preparation according to reaction B would hardly indicate the reduction of nitrogen to the +3 state of the hypochlorite structure. Moreover, an interesting analogy can be drawn to the reaction of phthalic anhydride with PCl_5 , in which the chlorine atoms are directed to the two carbon atoms (corresponding to the two nitrogen atoms in N_2O_5 .)



2. The presumption that chlorine can not have electropositive character as the chloride of nitric acid was not established by Schmeisser. There is, every reason to believe that it could be positive if its structure is represented as follows:



Since the nitrogen would tend to be positive due to the donation of two of its electrons to one of the oxygen atoms, it could attract the electrons in the $\text{N}-\text{Cl}$ bond, leaving the chlorine electropositive.

This is a continuation of the work done in the previous report. The results of the experiments are given in the following tables. The first table shows the results of the experiments on the effect of the concentration of the solution on the rate of reaction. The second table shows the results of the experiments on the effect of the temperature on the rate of reaction. The third table shows the results of the experiments on the effect of the catalyst on the rate of reaction.

III. 1. (continued)

1. The concentration of the solution was varied from 0.1 to 1.0 M. The results are given in the following table.

2. The temperature was varied from 20°C to 40°C. The results are given in the following table.

3. The catalyst was varied from 0 to 1.0 M. The results are given in the following table.

4. The concentration of the solution was varied from 0.1 to 1.0 M. The results are given in the following table.

5. The temperature was varied from 20°C to 40°C. The results are given in the following table.

6. The catalyst was varied from 0 to 1.0 M. The results are given in the following table.

7. The concentration of the solution was varied from 0.1 to 1.0 M. The results are given in the following table.

8. The temperature was varied from 20°C to 40°C. The results are given in the following table.

9. The catalyst was varied from 0 to 1.0 M. The results are given in the following table.

10. The concentration of the solution was varied from 0.1 to 1.0 M. The results are given in the following table.

11. The temperature was varied from 20°C to 40°C. The results are given in the following table.

12. The catalyst was varied from 0 to 1.0 M. The results are given in the following table.

13. The concentration of the solution was varied from 0.1 to 1.0 M. The results are given in the following table.

14. The temperature was varied from 20°C to 40°C. The results are given in the following table.

15. The catalyst was varied from 0 to 1.0 M. The results are given in the following table.

16. The concentration of the solution was varied from 0.1 to 1.0 M. The results are given in the following table.

17. The temperature was varied from 20°C to 40°C. The results are given in the following table.

18. The catalyst was varied from 0 to 1.0 M. The results are given in the following table.

3. In addition reactions of NO_2Cl with substituted aliphatic olefins (reactions H and J) it appears that the chlorine atom has an electronegative character, if the analogy is drawn to the addition of hydrohalogen compounds to similar olefins.

Conclusion: It may be concluded, therefore, that the chlorine in NO_2Cl may display either electropositive or electronegative character in chemical reactions; that either the hypochlorite or acid chloride structure are commensurable, so far as these reactions are concerned; but that the methods of preparation favor the acid chloride form.

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SULFIDES OF PHOSPHORUS

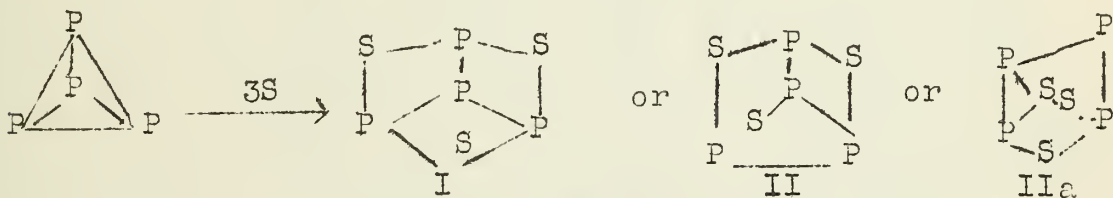
L. F. Audrieth

December 7, 1948

Only four sulfides of phosphorus are definitely known: P_4S_3 , P_4S_5 , P_4S_7 and P_4S_{10} . All may be prepared by direct reaction of phosphorus and sulfur, although care must be taken if the higher sulfides are to be produced 1) to assure complete reaction and 2) to avoid decomposition (dissociation) of intermediate sulfides. In spite of references in the organic literature to P_4S_6 (P_2S_3), this compound has never been prepared and is unknown.

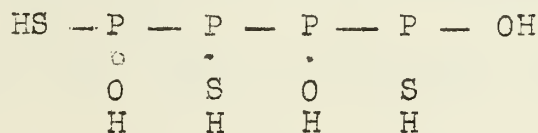
P_4S_3 is known in the older literature as "phosphorus sesqui-sulfide". It is relatively non-toxic and has displaced white phosphorus in the match industry, which is still the major consumer of this chemical commodity. Phosphorus (V) sulfide, P_4S_{10} is widely used for the preparation of thio-; thiono- phosphoric acid derivatives of organic compounds which are used as oil additives, flotation agents and insecticides. When fused with P_4O_{10} there is obtained the mixed oxy-sulfide, $P_4S_4O_6$, a new chemical intermediate which is now potentially available for the first time: $3P_4O_{10} + 2P_4S_{10} \longrightarrow 5P_4S_4O_6$.

The structure of P_4S_3 has never been elucidated heretofore. On the basis of the tetrahedral structure for in the P_4 molecule, Pernert (1) assumes that the initial reaction between phosphorus and sulfur involves merely the production of a less strained molecule namely P_4S_3 .

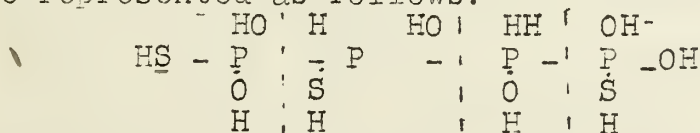


Structure II seems preferred and may be represented also as IIa. Addition of two or four thiono atoms give P_4S_5 and P_4S_7 , respectively.

Hydrolysis would involve initial attack on sulfur atoms to give a hypothetical intermediate:



and further hydrolysis with rupture of $P - P$ linkages could be represented as follows:



The theoretical fragment $H_2P(OH)$ or H_3PO is not known, but might be expected to give PH_3 and H_3PO_2 . Thus, one mole of P_4S_3 on complete hydrolysis should give 2 moles H_3PO_3 , 1.5 moles H_3PO_2 and 0.5 moles PH_3 . Experimental results approximate these theoretical requirements and are offered in support of the P_4S_3 structure.

References: J.C.Pernert and J.H.Brown - Paper presented at the Syracuse Symposium of Inorganic Chemistry, June 1948, to be published in the News Edition, 1949.

THE EXPLOSIVE TENDENCIES OF AMMONIUM NITRATE

John S. Wilson

December 14, 1948

I. Importance of ammonium nitrate

Large quantities of ammonium nitrate are produced annually for use in explosives and as a fertilizer. It is an important component of the "safe" explosives used industrially. The ease of production of the salt from atmospheric nitrogen and its high nitrogen content make it one of the leading fertilizers. The hygroscopic properties of ammonium nitrate have been overcome by coating the grains with substances such as petrolatum (1). Recent disasters have brought about renewed interest in the study and control of its explosive tendencies to ensure safety in its manufacture, transportation, and use.

II. Explosions and fires involving ammonium nitrate.

Prior to 1920 pure ammonium nitrate was not considered to be an explosive even though Berthelot (2) had studied its explosive decomposition as early as 1869. Since 1916 several explosions involving ammonium nitrate have occurred. These have been initiated either by other explosions or by heat along. The following detonations and fires have been reported in the literature:

A. Explosions - Initiated by detonation

1. 1918 - Morgan, N. J. (2). A shell loading plant burned and several warehouses containing ammonium nitrate exploded. The detonations were thought to have been initiated by high explosive shells projected from other parts of the plant as some warehouses burned with no explosions and only partial destruction of the ammonium nitrate.
2. 1921- Opau, Germany (3,4) 4500 tons of a mixture of ammonium nitrate and ammonium sulfate exploded. Blasting was being carried out in a stockpile to loosen the caked salt. Apparently the area in which the blast occurred was rich in ammonium nitrate.

B. Explosions - Initiated by heat

1. 1916 - Rapauno, N.J. (2). 4000 lbs. of ammonium nitrate exploded during the process of recrystallization by evaporation from spent TNT acids. Nitro bodies present in the melt were blamed.
2. 1916 - Oakdale, N.J. (2). An explosion similar to the one which had occurred at Rapauno with the same conditions existing.
3. 1924- Nixon, N.J. (5). Ammonium nitrate recovered from amolol exploded while being grained and coated. One half to one per cent TNT present was believed to have been responsible for the explosion.
4. 1925- Emporium, Pa. (6). Explosion while previously coated ammonium nitrate was being reworked.
5. 1932- Rapauno, N.J. (1). Explosion of ammonium nitrate containing .25% petrolatum and ammonium chloride.
6. 1936- Merano, Italy (1). Explosion in a neutralizer during the manufacture of ammonium nitrate. A piece of sacking was known to have fallen into the mixture and shortly afterward the temperature rose from a normal of 160 deg. to 190 deg. An hour later the mixture exploded.
7. 1944- USA (1). A wartime explosion of ammonium nitrate. Thought to have been caused by oil introduced from the compressor used to furnish compressed air for agitation during the evaporation of an ammonium nitrate solution.

8. 1947- Texas City (7). Explosion of ammonium nitrate laden French ship "Grandcamp". The next day a second ship exploded. Later during the year another ship exploded under similar circumstances in a French harbor.
- C. Fires with no resulting explosion.
 1. Barksdale, Wis. (2). A building containing 30,000 lbs. of ammonium nitrate in barrels, burned completely. Some of the nitrate was unconsumed.
 2. 1920- Brooklyn Pier (2). The steamship "Hallfried" with a cargo of 4,320,000 lbs. of ammonium nitrate partially burned. After the fire 1,944,500 lbs. of nitrate was recovered.
 3. 1925- Muscle Shoals (6). Two railway cars loaded with ammonium nitrate burned.
 4. 1947- In the proceeding 4-5 years ten to twelve wooden box-cars containing ammonium nitrate burned. The railroads do not use steel cars for the transportation of ammonium nitrate (8).

III. The nature of explosives and explosions.

One definition of an explosive is a substance which, when subjected to sufficient initial impulse, undergoes very rapid chemical transformation with the evolution of heat and the release of gases which tend to occupy a volume much greater than that of the original substance (9). The reaction may be an almost instantaneous combustion or a chemical decomposition. If an oxidation reaction liberates heat faster than the heat escapes the temperature rises and the reaction rate increases. The limit is determined by the supply of oxygen and if the substance contains available oxygen the reaction becomes an explosion (10). The high explosives are those which undergo detonation (11). A certain minimum amount of energy is required to initiate the detonation of a high explosive. If the energy threshold is low such that the material is sensitive to impact, friction, or flame, the explosive is termed an "initiator". These are used to detonate the more insensitive bursting charge explosives. In the detonation of a high explosive there are at least three phases (12). First there must be initiation of the grains of the explosive. Secondly the chemical reaction initiated must be propagated through the grain. Third the detonation must be transmitted to adjacent grains by the shock wave produced. The power of the explosion depends upon the energy of the reaction, and the nature of propagation of the shock wave. If the shock wave is transmitted with decreasing intensity the explosion will die out. If the shock wave is transmitted with increasing intensity and velocity the detonation is very violent.

IV. The explosion of ammonium nitrate.

Ammonium nitrate is classed as a bursting charge; it is very difficult to initiate its detonation when in a pure state. (1) Most early attempts to explode the nitrate by heating alone failed because the starting mass was too small and the heat evolved escaped to the surroundings.

Saunders (13) reported heating the pure salt to 300 deg. C. Red fumes were given off and an explosion occurred. Analysis of the products of the explosion indicated that the reaction proceeds in accordance with the equation:



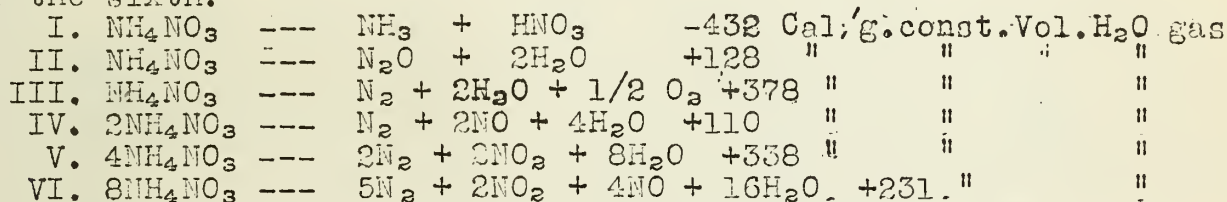
Sherrick (1), Jones (14), and Gawthrop (15) produced violent explosions of ammonium nitrate under confinement in steel tubes both by heating and by explosive initiation.

Munroe (5) attempted to detonate unconfined ammonium nitrate with blasting gelatine and reported that it propagated its own shock wave but with decreasing force and velocity.

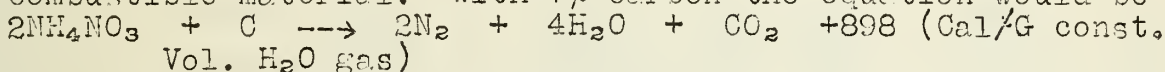
Cook (16) found that organic impurities greatly increased the force of the explosion, especially under conditions of confinement. He found 1% petrolatum to have a greater effect than the same amount of TNT. Commercial fertilizers such as those which exploded at Texas City may contain as much as 2% petrolatum. The Bureau of Mines (17) detonated samples of fertilizer from Texas City by heat along.

Saunders (13) reported 1% chloride ion impurity increased the rate of evolution of gas from ammonium nitrate to the same extent as a temperature rise of 25-30 deg. C.

The products of the decomposition of ammonium nitrate depend upon the temperature of the reaction. The first five equations are those given by Berthelot (1). Saunders (13) is responsible for the sixth.



Reaction I occurs up to 190 deg. C. and II above 200 deg. C. Number III is the reaction which occurs especially in the presence of combustible material. With 7% carbon the equation would be



Equations IV, V, and VI represent possible reactions during the explosive decomposition.

V. Conclusions

Ammonium nitrate is an explosive but requires a very high energy of initiation. Detonation is facilitated by conditions of confinement, large bulk, heat, and impurities.

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AMMONIUM AND SUBSTITUTED AMMONIUM RADICALS

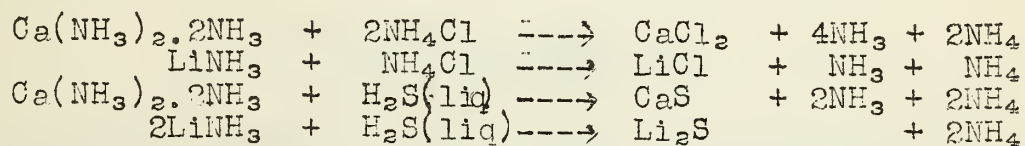
Eugene P. Bertin

December 14, 1948

The parallelism in chemical behavior of hydrogen and the ammonium group to that of the alkali metals has occasioned much experimentation and speculation. It was once thought by many that when obtained, solid hydrogen would prove to be a metallic substance; this, we know, has not been borne out (see, however (27)). In the case of the ammonium radical, on the other hand, considerable evidence has been amassed that, could we but isolate it, we should indeed find it to be metallic. A review of the endeavors that have been made along this line is the subject of this discussion.

I. The Existence of Free NH_4

The early work of Weil, who claimed that free NH_4 is obtained by the action under pressure of NH_3 gas on K and NH_4Cl (60), has long since been discredited and is of historical interest only. (22) Moissan, reasoning that NH_4 might be stable at very low temperatures, attempted to produce it at -70° to -75° using the reactions listed below, but found that the equivalent of the NH_4 expected appears as NH_3 and H_2 , showing the NH_4 to be unstable. (31)(32)(33)



Ruff concluded that NH_4 must be unstable at temperatures as low as -95° when he electrolyzed NH_4I in liq. $-\text{NH}_3$ at this temperature and observed no blue color such as appears when KI is electrolyzed. (45) Schlubach, however, found that if NH_4Cl in liq. $-\text{NH}_3$ is added slowly to a blue solution of K in liq. $-\text{NH}_3$ (both at -70°), the blue color disappears, yet only 37-75% of the H_2 calculated from the following equation is evolved:



After standing 3 hrs. at -70° , the filtered solution was found to react with I_2 (at -70° , which liq. $-\text{NH}_3$ does not), and to evolve the "missing" H_2 upon warming to -40° . S. concluded that such a solution contains NH_4 and that the absence of the blue color characteristic of alkali metal solutions might be due to dimerization. (49)

II. Ammonium Amalgam

A. Preparation

Ammonium amalgam (hereinafter: $\text{NH}_4\text{-Hg}$), apparently first prepared by Seebeck in 1808 (54), is prepared by 3 general methods:

1. Electrolysis of a pool of Hg in a hollowed block of solid $(\text{NH}_4)_2\text{CO}_3$ (54), NH_4Cl (14), $\text{CH}_3\text{COONH}_4$ (15), $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_3\text{PO}_4$ (18), etc., but not NH_4NO_3 . (61). The solids must be moist. (38)(40)

2. Electrolysis of solutions of NH_4 compounds (electrolytes) using a Hg cathode; e.g., aq. NH_4Cl (5)(18)(53), NH_4Br (36), $(\text{NH}_4)_2\text{CO}_3$ (18), or $(\text{NH}_4)_2\text{SO}_4$ (19); NH_4CNS in acetone; and NH_4Cl in glycerol. (38) Some moisture is necessary in the non-aqueous solvents. (40). One worker combined these methods, immersed a solid NH_4Cl cup containing the Hg cathode in

saturated aq. NH_4Cl . (3)

3. Treatment of amalgams with solutions of NH_4 compounds (14)(41), e.g., K-, Li-, Ba-, Sr-, or Ca-amalgam with NH_4CH_3 , but not Na amalgam (34)(42)(55)(61), which is, however, better than K amalgam with other NH_4 compounds. (6). $\text{NH}_4\text{-Hg}$ is also obtained by treating liq.- NH_3 solutions of NH_4Cl or NH_4I with Na amalgam. (34) See also (35).

B. Properties

1. Chemical

$\text{NH}_4\text{-Hg}$ is stable even in a vacuum at -80° , but begins to decompose at -30° . (34). Decomposition can be retarded in a H_2 atmosphere (5) or by pressure (36), accelerated by metallic Fe, Pt, or Al (7), NH_4NO_3 (61), EtOH , Et_2O , or shaking (13)(23) (34)(44) in agreement with the equation: $2\text{NH}_4\text{-Hg} \rightarrow 2\text{NH}_3 + \text{H}_2$. $\text{NH}_4\text{-Hg}$ displaces from aqueous solution Be^{++} and K^+ (9)(11) (55), Cu, Cd, and Zn at 0° (8), but not at 20° . (8) (23).

2. Physical

Calculated values for heat of formation, molar volume and density of solid NH_4 are (resp.) $-17,800 \text{ cal.mol}^{-1}$, 47.9 cm^3 , and 0.356 g. cm^{-3} (4). The electrode potential of $\text{NH}_4\text{-Hg}$ is probably very close to that of Na-Hg, (12)(21)(24)(26)(36)(59) (42). $\text{NH}_4\text{-Hg}$ emits electric charges on decomposing, predominately (+) but some (-). This phenomenon is discussed below. (1) (2)(10)(29). A photoelectric effect (less than for Na) has been observed. (46)

III. Substituted-Ammoniums

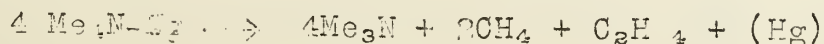
A. Early Work

Substituted ammonium amalgams were prepared as early as 1866 by Pfeil and Leffmann who treated a saturated solution of Me_4NCl with NaHg (38) and later by Wetherill who electrolyzed a globule of Hg on a filter paper soaked with "methyl-ammonium" oxalate solution. (62) Leblanc electrolyzed solutions of substituted ammonium salts using a Hg cathode and measuring the polarization potentials, inferred that $\text{MeNH}_3\text{-Me}_2\text{NH}_2\text{-}$, $\text{Me}_4\text{N-}$, and $\text{EtNH}_3\text{-}$ amalgams are relatively stable, $\text{Me}_3\text{NH-}$ and $\text{Et}_2\text{NH}_2\text{-}$ amalgams are relatively unstable, and $\text{Et}_3\text{NH-}$ amalgam is non-existent. (24) Palmer attributed the blue striae appearing at the Pt cathode of a cell in which electrolysis of Me_4NCl (or Me_4NOH) in liq. -NH_3 is taking place, to free Me_4N . (37)

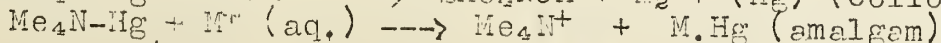
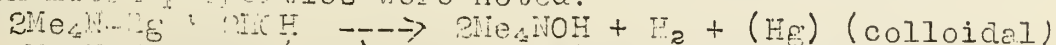
B. Substituted Ammonium Amalgams

A comprehensive study of these has been made by McCoy et al. (27)(28) Me_4N amalgam (hereinafter: $\text{Me}_4\text{N-Hg}$) was prepared by electrolysis at 0° to -34° (the lower the better) of Me_4NCl or Me_4NOH in abs. -EtOH using a Hg cathode and a Pt anode plated with Ag (to remove liberated Cl_2). Excess Hg was filtered off at 10° or less leaving the amalgam as a silver-white crystalline solid.

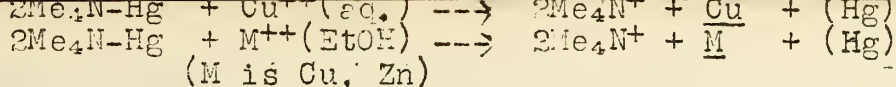
$\text{Me}_4\text{N-Hg}$ shows little change after several hours at 0° under CCl_4 is relatively stable at or under 10° , but decomposes rapidly at 20° :



Some chemical properties were noted:



(M is Na, K, Rb, Cs, NH_4)



$\text{Me}_4\text{N-Hg}$ also attacks abs. - EtOH, even, slowly, at -34° .

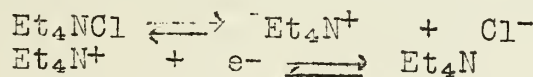
Some physical properties have been noted. The density decreases and the electrical resistance increases with Me_4N content. The radiation from the amalgam discharges only a (+)-charged electroscope, varies under constant conditions, is insensitive to day- or ultra-violet light, does not cloud photographic plates, is stopped by very thin Al, and is strongest when closest to the electroscope. Some cold, fresh crystals have been found not to emit, and in many cases, long after emission has ceased, a sample is still capable of decomposing H_2O . M. considers the phenomenon to be due to electrification of the gases escaping the amalgams observed by Lenard for air bubbled thru Hg. (25).

MeNH_3 amalgam was prepared by the electrolysis of MeNH_3 -salts in various solvents (H_2O (best), EtOH, MeOH, and glycerol) using a Hg cathode, was much less stable, and discharged both (+) - and (-)-electroscopes (the latter several times faster).

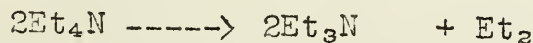
Me_2NH_2 and Et_4N may form very unstable amalgams, but none of the following salts showed any evidence of amalgam-formation: Me_3NHCl , EtNH_3Cl , PrNH_3Cl , trimethyl-iodomethyl-ammonium iodide, $\text{PhNH}_2\text{-HCl}$, $\text{PhNMe}_2\text{-HCl}$, phenylenediamine. HCl , PhNNCI , $\text{PyH}\cdot\text{HCl}$, Et_4PI , Me_4SbI , $\text{Me}_3\text{SI}\cdot\text{NH}_2\text{OH}\cdot\text{HCl}$, and $\text{NH}_2\text{NH}_2\cdot\text{HCl}$.

C. Solutions of Free Substituted Ammonium Radicals

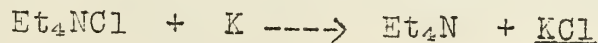
Schlubach et al. have made an equally comprehensive study of the solutions of free substituted ammonium radicals in liq.- NH_3 . (47)(48)(50)(51)(52) S. obtained blue solutions by electrolyzing solutions of Et_4NCl (or Et_4NI) in liq.- NH_3 at -75° . It was shown that these almost certainly contained free Et_4N :



at -78° the color persists several hours. Evaporation leaves only a trace of unreacted Et_4NCl (or Et_4NI). The liquid reacts with I and S to form (resp.) Et_4NI and a water-soluble sulfide, and with 2,6-Me₂-1,4-pyrone to give a characteristically-colored compound, these properties being analogous to those exhibited by K solutions in liq.- NH_3 . It does not, however, form a peroxide with O_2 nor an acetylide with C_2H_2 , as does K. It decomposes:

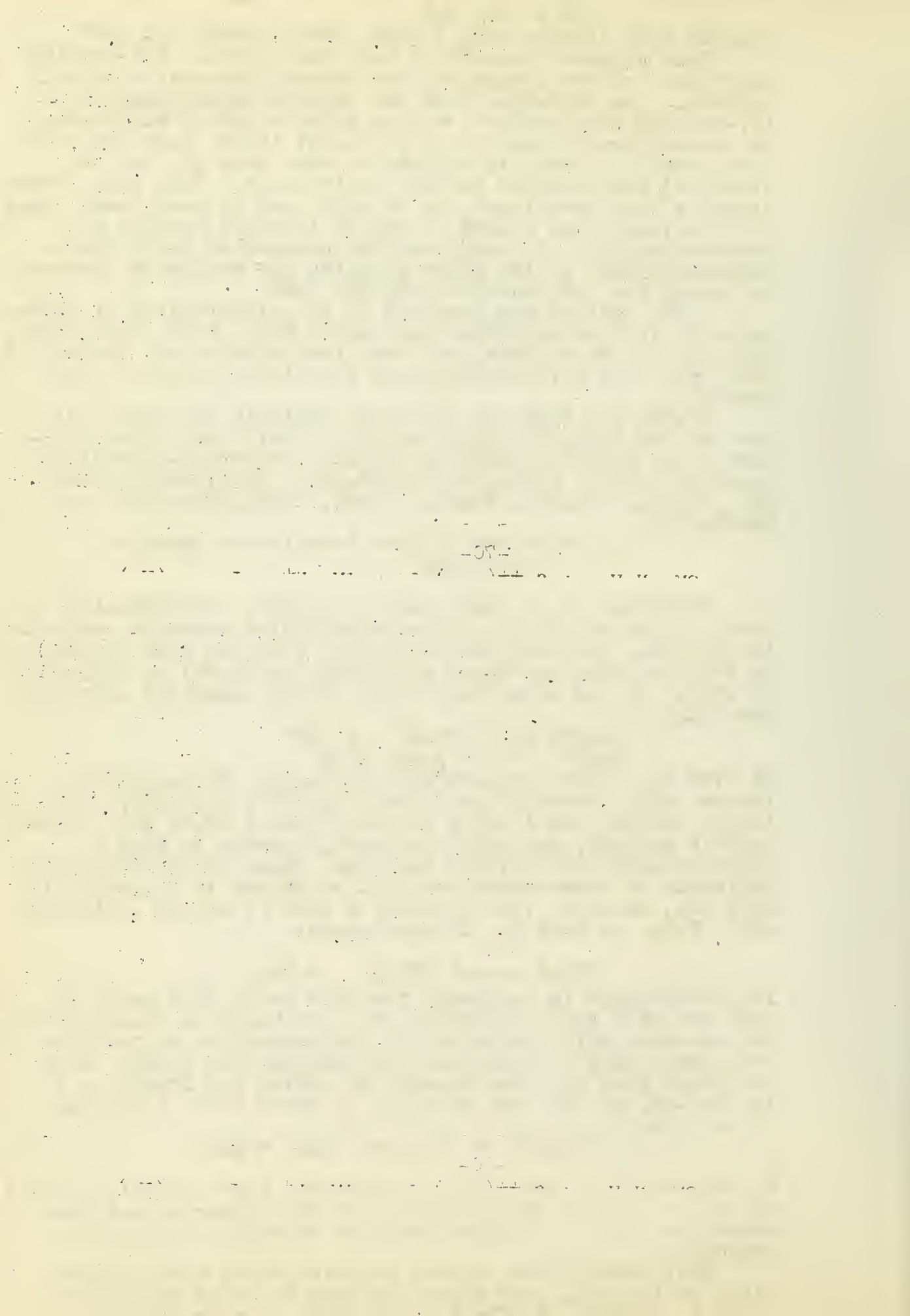


If electrolysis is prolonged the blue color will begin to fade and will fade completely in a few hours on standing, but the solution still exhibits all the properties of the blue one except that it decomposes differently (no Et_3N). This colorless form can also be made by adding dry Et_4NCl to K in liq.- NH_3 at -70° and allowing to stand until colorless (about 1 day).



S. Suggests that the blue and colorless forms contain (resp.) the mono- and dimeric radicals, but the latter do not dissociate on warming to give the blue solution, as might be expected.

Many substituted organic ammonium salts were electrolyzed in liq.- NH_3 , and tests for free radicals were made using 2 criteria: I. The formation of a blue solution, and



II. (more sensitive) the formation of a characteristically colored compound with 2, 6-Me₂-1,4-pyrrone. As the Et groups on Et₄N are replaced by PhCH₂-, Ph₃C-, Ph-, or H-, test I is negative with the first substitution; test II is very faint with the first and disappears completely with further substitution. NPr₄ is fairly stable. Et₄P, Et₄As, and Et₃S give no I test, but give a definite II test.

IV. Theory

Confronted with the problem of the nature of the radicals present in the amalgams and solutions we have just discussed, we find that work on this problem has been inadequate. NH₄-Hg, for instance, has at one time or another been considered a hydrogen-ammonia, analogous to K.NH₃, etc. (45), an ammoniacal Hg hydride (34), and a solution of metallic NH₄ in Hg (43)(59), but these theories have been discredited (55)(56)(57) in favor of others which regard NH₄-Hg as a true amalgam analogous to those of the alkali metals. (8) (24)(55)(56)(57).

An experiment by Reedy has neatly demonstrated the metallic nature of NH₄:Hg is poured into a beaker and a large glass tube suspended with its lower end well into the Hg, but not touching the bottom of the beaker. Aq. Na₂SO₄ is poured into the tube and aq. (NH₄)₂SO₄ into the beaker surrounding it. A C electrode is placed in each solution and electrolysis conducted with the Na solution (-). After awhile NH₄⁺ can be detected in the solution inside the tube. Reedy claims that in view of the insolubility of both NH₃ and NH₄⁺ in Hg, the only explanation is that NH₄ diffused in metallic form thru the Hg. (41)

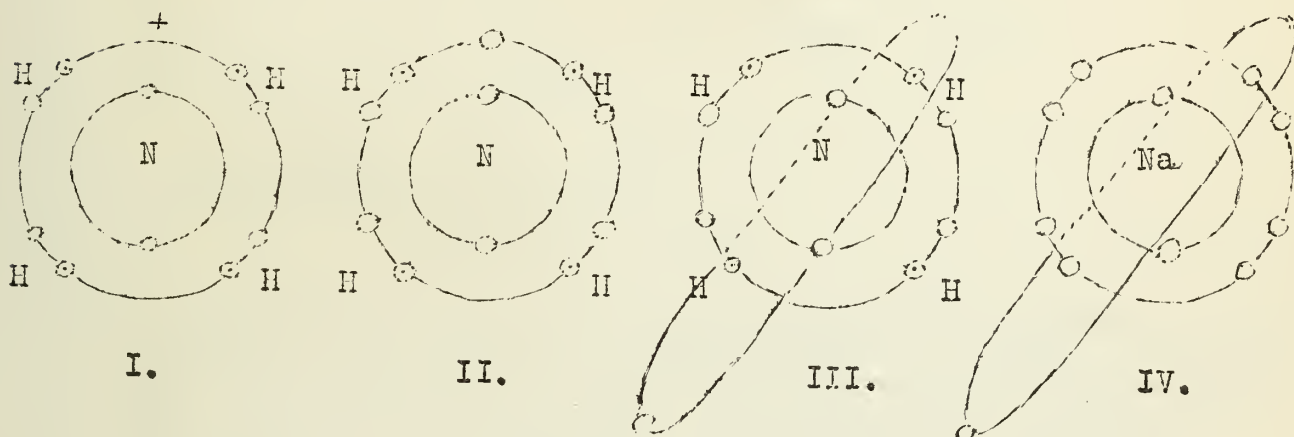
Deyrup, however, holds that the NH₄ in NH₄-Hg is completely dissociated into NH₄⁺ and e⁻, both more or less solvated. (15) McCoy proposes the hypothesis that the electrical neutralization of complex ions constituting the positive radicals of salts (by the introduction of electrons equal in number to the valence of the ion) will result in substances having metallic properties altho non-metallic constituents. (28) Schlubach recognizes the existence not only of ammonium, but also of phosphonium, sulfonium, and arsonium radicals differing from radicals hitherto known in that the valence of the central atom is one greater than in the most stable hydrogen compound, rather than one less (as, e.g., in R₃C., etc.).

It will be agreed that these considerations leave much to be desired with regard to solution of the fundamental problems presented by the observed facts we have reviewed. A comprehensive theory of the ammoniums should first present an acceptable structure for NH₄ (and NR₄) on a basis of which the following phenomena might be explained:

1. The emission and polarity of electric charges by the amalgams
2. The photoelectric effect observed in NH₄-Hg.
3. The observed decomposition products of the amalgams and liq. NH₃ solutions.
 - a. 2NH₄ (amal. or soln.) ----> 2NH₃ + H₂
 - b. 2Et₄N (soln.) ----> 2Et₃N + Et₂
 - c. 4Me₃N-Hg ----> 4Me₃N + 2C₂H₄ + C₂H₆ + (Hg)
4. Diffusion of NH₄ thru Hg (Reedy's experiment).
5. Analogies to alkali metal amalgams and liq.-NH₃ solutions.
6. Chemical behavior of liq.-NH₃ solutions.

7. Color phenomena in liq.-NH₃
 - a. NH₄: colorless; NEt₄: blue, becomes colorless.
 - b. The inconvertibility of the colorless to the blue form.
 - c. The identity of chemical behavior of the blue and colorless forms.
8. The order of stability (R₄N more stable than H₄N).
9. Difference in products of decomposition of colorless and blue forms of Et₄N solution in liq.-NH₃.

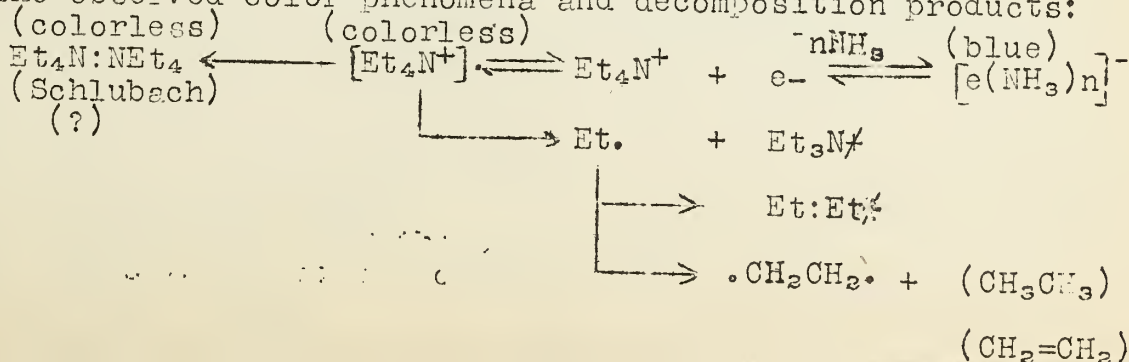
In writing a structure for NH₄ (or NR₄) one is immediately confronted with the unlikely aspect of the 9-electron nitrogen L shell (II) which is obtained by neutralizing NH₄⁺ ion (I) with an electron.

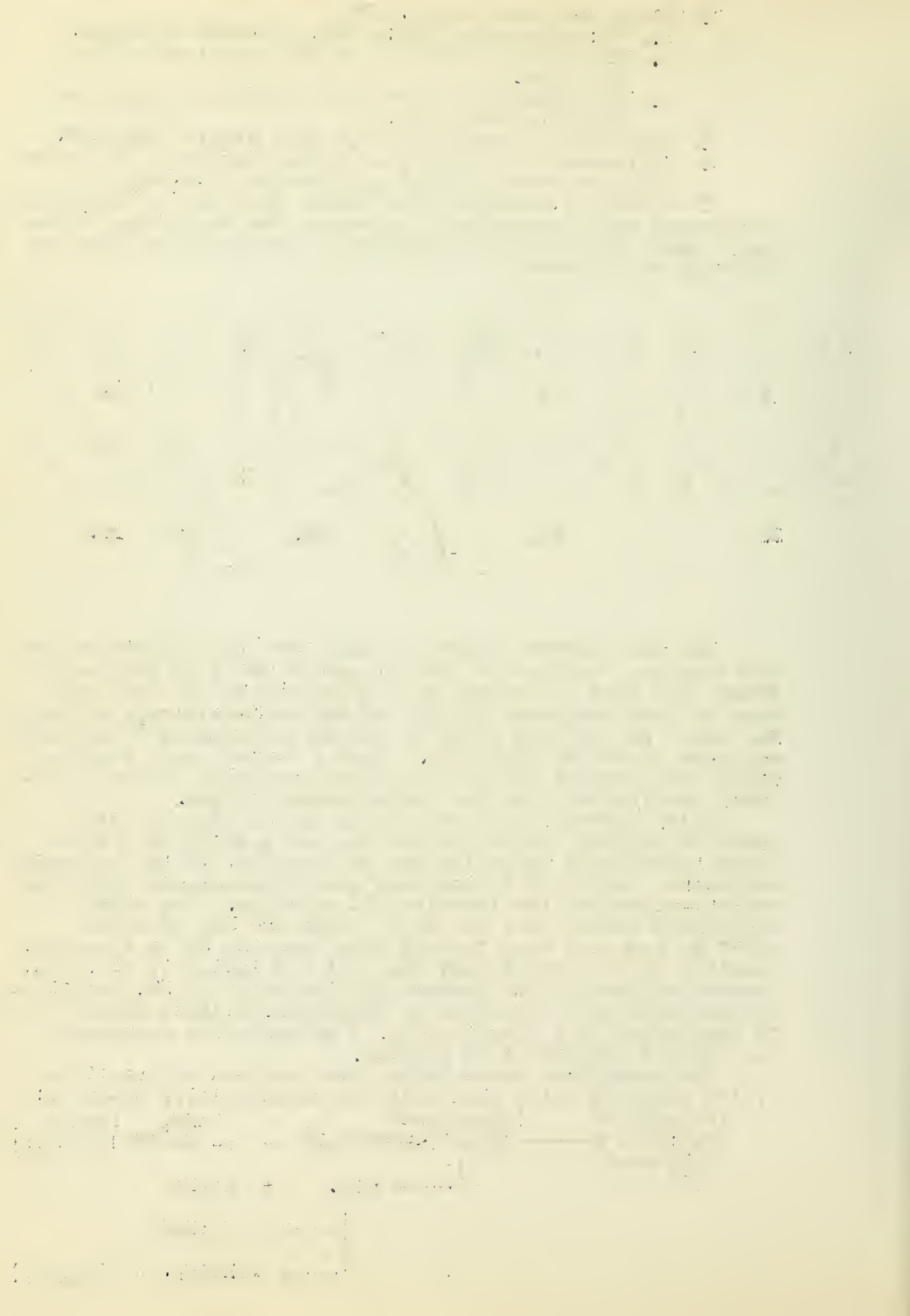


Let us, however, postulate that the "odd" electron does not occupy a position in the nitrogen L shell in the usual sense, but that it assumes a relationship to the NH₄⁺ core more or less analogous to that of the Na 3s electron to the Na core, giving what might be termed an ammonium "atom" (III) analogous to the Na atom (IV). Such a loosely held electron might well account for the metallic properties of the ammoniums, particularly for the photoelectric effect.

Note, however, that whereas in the Na atom all the positive charges are in the nucleus and a shell of 8 electrons immediately underlies the 3s electron, in the ammonium structure a shell of 8 electrons and 4 protons--the hydrogen nuclei--underlies the loosely-held electron. One might reasonably expect that for this reason the NH₄ electron might be somewhat more tightly held than the Na 3s electron, possibly to the extent that NH₄ will not ionize in liq.-NH₃, thereby explaining the absence of blue color of NH₄ solutions in this solvent as observed by Schulbach, without resort to assumption of a dimeric form, a satisfactory structure for which is difficult to imagine.

The mechanisms shown below give proposed explanations of the observed color phenomena and decomposition products:





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The Determination of Ionic Weights by Dialysis

Dale E. Jackson

January 4, 1949

I. The Development of the Method

A. The Theory

1. Diffusion as a background

If a solution is placed below the pure solvent in a cylindrical tube, the solute will move across the interface according to the following equation (24):

$$\frac{ds}{dt} = - Dq \frac{dc}{dx} \quad (1)$$

Where ds =moles of solute diffusing in unit time, dt =time, usually 1 day. D =diffusion coefficient, q =cross-sectional area, 1 cm.², dc =decrease in concentration with distance x (in the solvent), and dx =distance from the interface to a line in the solvent.

The relation between D and the weight of the solute particles (M) has been shown (24) to be $D \propto \frac{1}{M}$ constant. (2)

This equation is more useful in the following form:

$$(D_1)^2 M_1 = (D_2)^2 M_2 \quad (3) \quad \text{or} \quad M_1 = \left(\frac{D_2}{D_1} \right)^2 M_2 \quad (4)$$

It is apparent from equation (4) that an unknown particle weight may be determined by comparing its diffusion coefficient with that of a particle of known weight. For this purpose the solvent and solution alike must contain a foreign electrolyte at a concentration approximately ten times that of the species under study. The functions of the electrolyte are as follows (19)

- (1) to mask the electrostatic attraction between the ion under study and its partner,
- (2) to allow quicker diffusion of the ion by decreasing the water well around it, and
- (3) to decrease the dissociation of a complex ion.

This method has the following disadvantages:

- (1) The process is a very slow one.
- (2) The unknown and reference species must be stable for several days or weeks.
- (3) The cylinder must be kept free from physical shock during the entire period.
- (4) There can be no temperature change.

It has been found that the interface maybe replaced by a membrane which will maintain a certain degree of permeability. This process is called dialysis. It requires much less time than diffusion and eliminates the other disadvantages listed above

2. The equation for dialysis

The curve obtained by plotting the decrease in concentration of a dialyzing solute versus time is similar to that of the decay of a radioactive substance and similar phenomena (1a). It may be represented as follows:



1. The first part of the report is a summary of the work done during the year. It is a brief statement of the results of the work, and is intended to give a general idea of the progress made.

2. The second part of the report is a detailed account of the work done during the year.

The work done during the year has been of a general nature, and has been directed towards the improvement of the methods of working. It has been found that the present methods of working are not satisfactory, and that it is necessary to adopt new methods. The new methods have been adopted, and it is hoped that they will result in a more efficient and economical way of working.

(1) The first part of the work has been to determine the present methods of working, and to find out what is wrong with them. It has been found that the present methods are not satisfactory, and that it is necessary to adopt new methods.

(2) The second part of the work has been to determine the new methods of working, and to find out what is wrong with them. It has been found that the new methods are not satisfactory, and that it is necessary to adopt new methods.

(3) The third part of the work has been to determine the new methods of working, and to find out what is wrong with them. It has been found that the new methods are not satisfactory, and that it is necessary to adopt new methods.

(4) The fourth part of the work has been to determine the new methods of working, and to find out what is wrong with them. It has been found that the new methods are not satisfactory, and that it is necessary to adopt new methods.

(5) The fifth part of the work has been to determine the new methods of working, and to find out what is wrong with them. It has been found that the new methods are not satisfactory, and that it is necessary to adopt new methods.

(6) The sixth part of the work has been to determine the new methods of working, and to find out what is wrong with them. It has been found that the new methods are not satisfactory, and that it is necessary to adopt new methods.

(7) The seventh part of the work has been to determine the new methods of working, and to find out what is wrong with them. It has been found that the new methods are not satisfactory, and that it is necessary to adopt new methods.

(8) The eighth part of the work has been to determine the new methods of working, and to find out what is wrong with them. It has been found that the new methods are not satisfactory, and that it is necessary to adopt new methods.

(9) The ninth part of the work has been to determine the new methods of working, and to find out what is wrong with them. It has been found that the new methods are not satisfactory, and that it is necessary to adopt new methods.

(10) The tenth part of the work has been to determine the new methods of working, and to find out what is wrong with them. It has been found that the new methods are not satisfactory, and that it is necessary to adopt new methods.

3. The conclusion of the report is that the work done during the year has been of a general nature, and has been directed towards the improvement of the methods of working. It has been found that the present methods of working are not satisfactory, and that it is necessary to adopt new methods. The new methods have been adopted, and it is hoped that they will result in a more efficient and economical way of working.



The equation for such a curve is as follows:

$$C_t = C_0 e^{-\lambda t} \quad (5)$$

where C_t = concentration of solute in the solution at time t , C_0 = original concentration, and h = dialysis coefficient. Solving for h , the following expression is obtained (1b):

$$h = \frac{\log C_0 - \log C_t}{t \log e} \quad (6)$$

As with the diffusion coefficient, there exists a relation between h and the particle weight as follows:

$$L_1^2 M_1 = h_2^2 M_2 \quad (7)$$

or

$$M_1 = \left(\frac{L_2}{L_1} \right)^2 M_2$$

By determining the h value for a known or reference particle and that of an unknown, the weight of the latter may be determined.

B. Apparatus and Procedure (1q)

1. Apparatus

The necessary equipment consists essentially of a large, glass thermostat (5-6 liter capacity) above which is suspended a small dialyzer fitted with a stirrer. The bottom of the dialyzer consists of a membrane made of cellophane or cuprophane. The thermostat has a plywood cover into which are fitted the dialyzer, a thermometer, a mercury thermoregulator, a heating lamp, a stirrer, and a cold water pipe.

2. Procedure

In a typical run, 35 ml. of solution containing the unknown ion (usually 0.1M) are dialyzed for 1/2, 1, and 1 1/2 hour periods into 4 to 5 liters of solvent. Both the solution and solvent contain a ten-fold concentration of an indifferent electrolyte. A reference ion, $\text{CrO}_4^{=}$, $\text{S}_2\text{O}_3^{=}$, or $\text{Fe}(\text{CN})_6^{-3}$ (in acid solution) is then dialyzed under exactly similar conditions. The temperature is kept at $18 \pm 0.05^\circ \text{C}$.

With reference to equation (6) C_0 is known; C_t is determined, and λ is calculated for both known and unknown. The desired weight is then calculated according to equation (8).

C. A Further Theoretical Discussion

1. The effect of certain variables on λ

Variations in pH were determined qualitatively to have no effect (15b). The concentration of the foreign electrolyte was likewise found to cause no change in h in most instances, except when the central atom of a complex ion changed coordination number (17b). If, in a given dialyzer, the volume of solution is doubled, the time required to reach a given C_t value is halved. To measure this variable the term "specific surface" was devised (1b). It is defined as the number of cm^2 of membrane surface per cc. of solution. Since the area in the apparatus used by Brintzinger was 35 cm^2 , he used 35 cc. of solution, which made F equal to unity.

The following equation illustrates the relation between λ and the temperature (2):

$$\lambda_{T_1} = \lambda_T [1 / \alpha (T_1 - T)] \quad (9)$$

where α is the temperature coefficient.

The various factors may be expressed in conjunction with the dialysis equation as follows (17b):

1. The effect of various substances on the growth of the plant is as follows:

(a) The effect of water is that it is essential for the growth of the plant. Without water, the plant will die.

(b) The effect of light is that it is essential for the growth of the plant. Without light, the plant will die.

(c) The effect of carbon dioxide is that it is essential for the growth of the plant. Without carbon dioxide, the plant will die.

(d) The effect of oxygen is that it is essential for the growth of the plant. Without oxygen, the plant will die.

(e) The effect of nitrogen is that it is essential for the growth of the plant. Without nitrogen, the plant will die.

(f) The effect of phosphorus is that it is essential for the growth of the plant. Without phosphorus, the plant will die.

(g) The effect of potassium is that it is essential for the growth of the plant. Without potassium, the plant will die.

(h) The effect of calcium is that it is essential for the growth of the plant. Without calcium, the plant will die.

(i) The effect of magnesium is that it is essential for the growth of the plant. Without magnesium, the plant will die.

(j) The effect of sulfur is that it is essential for the growth of the plant. Without sulfur, the plant will die.

(k) The effect of iron is that it is essential for the growth of the plant. Without iron, the plant will die.

(l) The effect of zinc is that it is essential for the growth of the plant. Without zinc, the plant will die.

(m) The effect of copper is that it is essential for the growth of the plant. Without copper, the plant will die.

(n) The effect of manganese is that it is essential for the growth of the plant. Without manganese, the plant will die.

(o) The effect of boron is that it is essential for the growth of the plant. Without boron, the plant will die.

(p) The effect of molybdenum is that it is essential for the growth of the plant. Without molybdenum, the plant will die.

(q) The effect of chlorine is that it is essential for the growth of the plant. Without chlorine, the plant will die.

(r) The effect of silicon is that it is essential for the growth of the plant. Without silicon, the plant will die.

(s) The effect of selenium is that it is essential for the growth of the plant. Without selenium, the plant will die.

(t) The effect of cobalt is that it is essential for the growth of the plant. Without cobalt, the plant will die.

(u) The effect of nickel is that it is essential for the growth of the plant. Without nickel, the plant will die.

(v) The effect of vanadium is that it is essential for the growth of the plant. Without vanadium, the plant will die.

(w) The effect of chromium is that it is essential for the growth of the plant. Without chromium, the plant will die.

(x) The effect of manganese is that it is essential for the growth of the plant. Without manganese, the plant will die.

(y) The effect of iron is that it is essential for the growth of the plant. Without iron, the plant will die.

(z) The effect of copper is that it is essential for the growth of the plant. Without copper, the plant will die.

$$C_t = C_o e^{-\lambda t} \cdot \frac{F \cdot 1}{S_M (f) K}$$

Where S_M = strength of the membrane and $(f)K$ = a function of the concentration of certain foreign electrolytes. This equation is not used in calculating λ since the additional factors are constant for both the unknown and reference runs.

2. The importance of the membrane used.

Jander and Spandau (25) found λ values to decrease in relation to the diffusion constants of certain ions. They proposed that this was due to the small pore size of cellophane and cuprophane (10-40 μ A.), which slowed the dialysis of particles weighing over 200. They recommended the use of cellamembrane with a pore radius between 400 and 2000 μ A.

Brintzinger (26) published an exhaustive comparison of the aforementioned membranes, showing there to be little or no difference in their applicability.

3. The question of ion hydration

A difference in degree of hydration, either physical or chemical, will cause inaccuracies in the comparison of reference and unknown anionic weights. That the possibility of such differences is remote was demonstrated (13a) by determining the weight of $\text{Co}(\text{NH}_3)_6^{+3}$ with reference ions of greatly varying weight, charge, and nature.

4. Non-uniform particles (13a)

If particles of varying size and weight are present, the smaller ones will diffuse more rapidly and the solution will become enriched in the larger variety. Such behavior is betrayed by a decrease in λ values with increasing dialysis periods.

Critical Review by Jander and Spandau (25)

These investigators stressed the need for absolutely reproducible stirring speeds. They found only sodium nitrate (0.5 to 8.0N) to cause no change in λ when used as a foreign electrolyte. The effects of osmosis and filtration proved to be negligible.

III. Experimental

The ionic weight determinations carried out by Brintzinger will be discussed under as general headings as possible.

A. Complex Anions

1. Hydroxo (23b)

Ion	Calc.wt.	Obs.wt.			Conditions		
		cellophane	cellamembrane				
$\text{Sb}(\text{OH})_4^-$	190	192	195	$\text{CrO}_4^{=}$	reference;	2.5N	KOH
$\text{Sb}(\text{OH})_5^-$	224	222	226	"	"	"	"
$\text{Ge}(\text{OH})_6^{=}$	175	173	173	"	"	"	"
$[\text{Al}(\text{OH})_5]^-$	224	218	222	"	"	"	"
or							
$[\text{AlO}(\text{OH})_4]^{=}$	222	218	222	"	"	"	"

3. Organic Anions

Ion	Calc. wt.	Obs. wt.	Conditions	Ion	Calc. wt.	Obs. wt.	Conditions
Ndmel_3^{-3}	450	447	$\text{Fe}(\text{CN})_6^{-3}$ ref.	$\text{Co}(\text{HCOO})_5^{-4}$	329	331	$\text{S}_2\text{O}_3^{2-}$ ref.
$[\text{Femel}_2]_2^{-4}$	520	520	2N ammonium	$\text{Cr}_2(\text{OH})_2(\text{HCOO})_6^{+}$	460	463	2N HCOONH_4
Thmel_4^{-4}	340	650	malonate	$\text{Cu}(\text{HCOO})_4^{-2}$	244	233	5N HCOONH_4
$[\text{Fe}(\text{C}_2\text{O}_4)_2]_2^{-4}$	464	466	$\text{S}_2\text{O}_3^{2-}$ ref.	$\text{UO}_2(\text{OAc})_3^{-}$	477	446	$\text{S}_2\text{O}_3^{2-}$ ref.
$\text{VO}(\text{C}_2\text{O}_4)_2^{-2}$	243	244	2N $(\text{NH}_4)_2\text{C}_2\text{O}_4$				1.5N KOAc
$[\text{Th}(\text{C}_2\text{O}_4)_4]_2^{-8}$	1168	1165	(8)				(18)

3. Cyano

Ion	212	212	CrO_4^{2-} ref.	$\text{W}(\text{CN})_8^{-4}$	392	316	CrO_4^{2-} ref.
$\text{Fe}(\text{CN})_6^{-3}$	428	429	2N KCN	$\text{Cd}(\text{CN})_2^{-2}$	216	217	2N KCN
$[\text{Fe}(\text{CN})_6(\text{H}_2\text{O})_2]^{-4}$	160	160	(3b)				(36)
$\text{Ag}(\text{CN})_2^{-}$	168	166		$[\text{Fe}(\text{CN})_5(\text{AsO}_2)(\text{H}_2\text{O})_2]^{-4}$	617	629	(12)
$\text{Cu}(\text{CN})_4^{-3}$							

The tendency of ferrocyanide complexes to hydrate was reflected in their $\text{Mn}(\text{II})$ and $\text{Co}(\text{II})$ analogs.

4. Thioanions

$\text{Ag}(\text{SCN})_2^{-}$	224	229	$\text{S}_2\text{O}_3^{2-}$ ref.	$[\text{Mn}(\text{SO}_4)_2]_2^{-4}$	494	483	CrO_4^{2-} ref.
$\text{Fe}(\text{SCN})_6^{-3}$	404	383	2-5N HSCN	$[\text{Fe}(\text{SO}_4)_2]_2^{-4}$	433	456	2N Na_2SO_4
$\text{Fe}(\text{SCN})_4^{-2}$	288	282	(3)	$[\text{Fe}(\text{SO}_4)_2]_3^{-3}$	744	749	(3c)
$\text{ThO}(\text{SCN})_6^{-4}$	596	582					
$[\text{Cu}(\text{S}_2\text{O}_3)_2]_2^{-2}$	351	354	CrO_4^{2-} ref.	$[\text{Ag}(\text{S}_2\text{O}_3)_2]_2^{-2}$	440	ca 440	Dilute solution
$[\text{Ti}(\text{S}_2\text{O}_3)_2]_2^{-2}$	632	634	2N $\text{Na}_2\text{S}_2\text{O}_3$	$[\text{Ag}(\text{S}_2\text{O}_3)_2]_2^{-10}$	888	ca 888	Above 20 g/l
$\text{Fe}(\text{S}_2\text{O}_3)_3$	392	406	(14)				$\text{Ag}_2\text{S}_2\text{O}_3$ and 380 g/l $\text{Na}_2\text{S}_2\text{O}_3$

The observed weight is closer to that of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{+}$ (384).

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Journal of Management Studies, 19(1), 67-80.

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B. Complex Cations
1. Aquo

Ion	Calc. wt.	Obs. wt.	Conditions	Ion	Calc. wt.	Obs. wt.	Conditions
$\text{Li}(\text{H}_2\text{O})_5^+$	97	92	$\text{S}_2\text{O}_3^{2-}$ and CrO_4^{2-} = ref.	$\text{Al}(\text{H}_2\text{O})_6^{3+}$	351	359	(same as other column)
$\text{Na}(\text{H}_2\text{O})_5^+$	77	73	NO_3^- solutions (4e)	$\text{La}(\text{H}_2\text{O})_6^{3+}$	247	235	
K^+	39.1	39.5		$\text{Th}(\text{H}_2\text{O})_{12}^{4+}$	448	454	
$\text{Be}(\text{H}_2\text{O})_2^{+2}$	225	232		$\text{Cr}(\text{H}_2\text{O})_{15}^{3+}$	322	321	
$\text{Ca}(\text{H}_2\text{O})_6^{+2}$	148	150		$\text{Fe}(\text{H}_2\text{O})_{18}^{2+}$	380	381	
$\text{Sr}(\text{H}_2\text{O})_4^{+2}$	160	160		$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	134	171	
Ba^{+2}	137	135		(Same for divalent Mn, Co, Ni, and Cu)			

$\text{Co}(\text{NH}_3)_6^{+3}$	161	160	$\text{S}_2\text{O}_3^{2-}$ = ref. (4b)	$\text{Cr}(\text{NH}_3)_6^{+3}$	154	155	$\text{S}_2\text{O}_3^{2-}$ = ref. (11a)
$\text{Co}(\text{NH}_3)_4\text{H}_2\text{OBr}^{+2.5}$	225	221	NaNO_3 soln. (7b)	$[\text{Co}(\text{NH}_3)_6]^{+6}$	478	476	2N NaNO_3
$\text{Cu}(\text{NH}_3)_4^{+2}$	132	131		$[\text{Co}(\text{NH}_3)_2\text{en}_2]^{+6}$	426	424	$\text{S}_2\text{O}_3^{2-}$ = ref. (21)
(Only in acetate solution)				$[\text{Co}(\text{NH}_3)_2\text{enCl}_2]^{+2}$	448	446	$2\text{N NH}_4\text{Cl}$

C. Aggregation and Hydration of Oxy-anions

1. Inorganic Polymers (9)

pH	Ion	Calc. wt.	Obs. wt.	Results of Titration
8.0 - 7.0	MoO_4^{2-}	160	160	A Na_2MoO_4 solution gave breaks at pH values of 6.4 and 5.2
6.0	λ values varied; several species present			CrO_4^{2-} = ref., 1N Na_2SO_4
5.0-1.5	$\text{Mo}_6\text{O}_{20}^{6-}$	896	899	
	Mo_6O_{21}	912		

8.0-7.5	$\text{W}_6\text{O}_{21}^{6-}$	248	248	
7.0-6.0	$\text{W}_6\text{O}_{20}^{6-}$	1440	1440	
	$\text{W}_6\text{O}_{21}^{6-}$	1494	1435	
5.0-4.5	$\text{W}_{12}\text{O}_{38}^{4-}$	2816	2713	
	$\text{W}_{12}\text{O}_{39}^{4-}$	2832		

A Na_2WO_4 solution gave breaks at pH values of 7.2 and 5.2

CrO_4^{2-} = ref., 1N Na_2SO_4

pH	Ion	Calc. wt.	Obs. wt.	Conditions
14.0 - 12.2	$\frac{VO_4(H_2O)_6^{-3}}$	223	228	CrO ₄ = ref., .25 N Na ₂ SO ₄ (10)
12.0	λ values vary, aggregation occurring			
11.0 - 10.0	$V_{2O_7}(H_2O)_6^{-4}$	322	320	
9.0	further aggregation			
8.8 - 7.0	$V_{4O_{13}}^{-6}$	412	416	

2. Miscellaneous

Ion	Calc. wt.	Obs. wt.	Conditions	Calc. wt.	Obs. wt.	Conditions
$AsS_4(H_2O)_2^{-3}$	239	245	S_2O_3 = ref.	235	230	CrO ₄ = ref.
$SnS_4(H_2O)_2^{-4}$	283	288	2N (NH ₄) ₂ S or	183	181	KOH soln. (5)
GeS_3^{-2}	169	170	2N NH ₄ HS			

The nature of arsenate and phosphate ions was studied over broad pH ranges.

pH	Ion	Calc. wt.	Obs. wt.	Conditions
14.2	$AsO_4(H_2O)_1^{-3}$	463	463	S_2O_3 = ref.
14.0	$AsO_4(H_2O)_1^{-3}$	355	361	1.5N KCl (15c)
13.0-11.0	non-uniform λ values			
10.0-8.0	$H_2AsO_4(H_2O)_6^{-3}$	248	242, 243, 248	
7.0	non-uniform λ values			
6.0	$H_2AsO_4(H_2O)_3^{-3}$	195	192	
5.0-4.0	$H_2AsO_4(H_2O)_2^{-2}$	177	173, 179	Fe(CN) ₆ = ref.
3.0	non-uniform λ values			
14.0	$PO_4(H_2O)_1^{-3}$	383	378	S_2O_3 = ref.
11.0 - 9.0	$HPO_4(H_2O)_2^{-2}$	240	238, 234	KCl soln. (15c)
5.0 - 2.0	$H_2PO_4(H_2O)_4^{-1}$	169	167-170	Fe(CN) ₆ = ref.

D. Ions with a Second Coordination Sphere

Ion	Calc. wt.	Obs. wt.	Conditions
$\text{Co}(\text{NH}_3)_6(\text{SO}_4)_4^{-5}$	545	541	$\text{S}_2\text{O}_3^{2-}$ ref. (7a)
$\text{Co}(\text{NH}_3)_4\text{CO}_3(\text{SO}_4)_4^{-7}$	571	572	4N $(\text{NH}_4)_2\text{SO}_4$
$\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}(\text{C}_2\text{O}_4)_4^{-5}$	514	519	3N $\text{K}_2\text{C}_2\text{O}_4$
$(\text{Coen}_3)_2(\text{SO}_4)_4^{-2}$	862	867	4N $(\text{NH}_4)_2\text{SO}_4$ (11b)
$(\text{Coen}_3)_2(\text{HPO}_4)_4^{-2}$	862	849	3N K_2HPO_4 (11c)
$(\text{Copn}_3)_2(\text{SO}_4)_4^{-2}$	946	964	$(\text{NH}_4)_2\text{SO}_4$ (16b)
$\text{Co}(\text{NH}_3)_4\text{SO}_4\text{F}_4^{-3}$	299	298	$\text{S}_2\text{O}_3^{2-}$ ref. (13b)
$(\text{Coen}_3)_2(\text{HAsO}_4)^{-2}$	1038	1071	CrO_4^{2-} ref. (13c)
			2N K_2HAsO_4
$\text{Fe}_3(\text{OH})_2(\text{OAc})_6(\text{SO}_4)_4^{-7}$	939	952	1.5N $(\text{NH}_4)_2\text{SO}_4$ (16a)

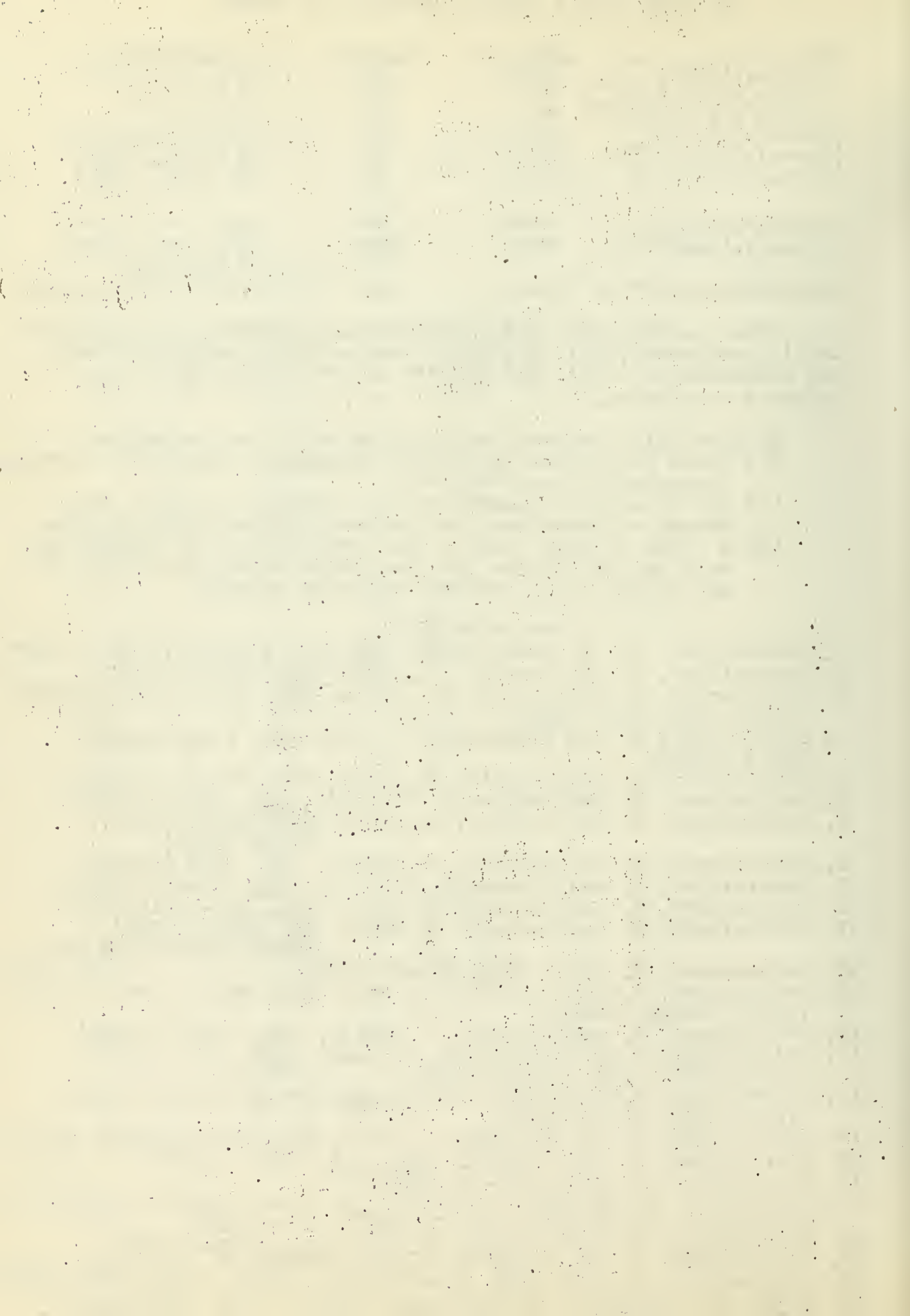
Other anions which enter into the second sphere are malonate (20b), succinate (20c), hydrogen citrate (20d), selenate (20c), and ferrocyanide (16c). The dimeric nature of $(\text{Coen}_3)_2^{+6}$ was apparent throughout.

In conclusion the following points should be remembered:

- (1) Since the method is one of comparison, many of the seeming inaccuracies are obviated.
- (2) The principal weakness of the method lies not in the theory or procedure, but in the interpretation of data.
- (3) A study of each metal cation over a broad pH range would be more informative than measurements on the cation at one pH and on the hydroxo-anion at another.

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Jan. 11, 1949

B. P. Block

A. Silver

1. Investigation of the reported disproportionation of silver (I) to silver (0) and silver (II).

Nakatsuka has found that silver (I) acetate reacts with 8-hydroxyquinoline at 65°C to give bis (8-quinolinato) silver (II) and metallic silver (4). His proof is based on the fact that one equivalent of his product reacted with seven equivalents of bromine rather than the eight expected for the corresponding silver (I) compound. Although the preparation of both the silver (I) compound, a yellow solid, and the reported silver (II) compound, a green solid, could be repeated, the bromine titration of the green solid could not be repeated; furthermore, the green solid was found to be diamagnetic although silver (II) compounds are paramagnetic. The two forms prepared by Nakatsuka are apparently both silver (I) compounds of 8-hydroxyquinoline and are probably the same forms reported by Hein and Regler. The latter investigators found that the yellow 8-hydroxyquinolinato of silver (I) could be changed to a green 8-hydroxyquinolinato of silver (I) upon crystallization from ammonium hydroxide (3).

Quinolinic acid complex

2. Bis (quinolinato) silver (II) has been prepared and studied more completely than in an earlier study (1). The structures proposed in the previous investigation are not as probably as coordination through the nitrogen and one carboxyl group of each quinolinic acid.

B. Gold

O-Phenanthroline complexes

1. Chloroauric acid reacts with o-phenanthroline to give a compound $\text{Au}(\text{o-phen})\text{Cl}_3$. Metathetical reactions show that the cation in aqueous solutions of this solid is $[\text{Au}(\text{o-phen})\text{Cl}_2]^+$ which means the compound should be formulated as $[\text{Au}(\text{o-phen})\text{Cl}_2]\text{Cl}$. Other compounds isolated containing this cation were the nitrate and chloroaurate. The latter compound was prepared by combining aqueous solutions of chloroauric acid and $[\text{Au}(\text{o-phen})\text{Cl}_2]\text{Cl}$ and has the empirical formula $\text{Au}_2\text{Cl}_5(\text{o-phen})$. In the literature it has been the custom to assign a bridging role to the bidentate group in binuclear molecules such as this. However, an investigation of the molecular dimensions involved shows that the distance between the nitrogens in the o-phenanthroline is 2.86Å whereas the sum of the radii of two gold atoms is 2.80Å which makes it very unlikely that the o-phenanthroline is acting as a bridging group. When the method of preparation is also considered, it is probably that the structure is $[\text{Au}(\text{o-phen})\text{Cl}_2][\text{AuCl}_4]$.

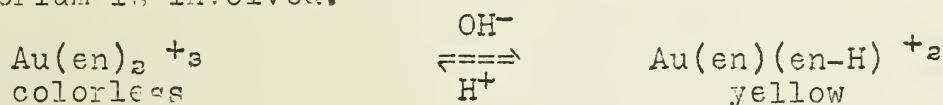
When potassium bromide is added to an aqueous solution of the dichloro (o-phenanthroline) gold (III), a precipitate is formed which seems to be $\text{Au}(\text{o-phen})\text{Br}_2 \cdot \text{Br}$.

Dipyridyl complexes

2. An alcoholic solution of dipyridyl added to a solution of chloroauric acid gives a compound which corresponds to $\text{Au}_2\text{Cl}_5(\text{dipy})$. Further treatment with dipyridyl seems to form $\text{Au}(\text{dipy})\text{Cl}_3$ although the latter could not be isolated in pure form and lost dipyridyl extremely readily to revert to the binuclear compound. If potassium bromoaurate is substituted for the chloroauric acid, the compound $\text{Au}_2\text{Br}_5(\text{dipy})$ is formed. Although there is no direct evidence for the structures of these compounds, they are provisionally formulated analogously to the o-phenanthroline complexes.

3. Ethylenediamine complexes

Gibson and Colles have reported that potassium bromoaurate and ethylenediamine form $\text{Au(en)}_2\text{Br}_3$ (2), but the present investigation did not confirm their work. Instead, it was found that the product was Au(en)(en-H)Br_2 . The addition of ethylenediamine to an ethereal solution of chloroauric acid forms a white solid, $\text{Au(en)}_2\text{Cl}_3$, which is extremely soluble in water. Treatment of a concentrated solution of this compound with a concentrated solution of potassium bromide at 5°C formed $\text{Au(en)}_2\text{Br}_3$, a light yellow, crystalline material. Determination of ionic halides per gold in aqueous solutions of the compounds and also metathetical reactions of the compounds indicate that the compounds should be formulated as $[\text{Au(en)(en-H)}]\text{Br}_2$, $[\text{Au(en)}_2]\text{Cl}_3$, and $[\text{Au(en)}_2]\text{Br}_3$, respectively. One equivalent of acid is accepted by an aqueous solution of Au(en)(en-H)Br_2 while one equivalent of base reacts with a solution of $\text{Au(en)}_2\text{Cl}_3$. The color changes and pH changes noted in these acid-base reactions show that the following equilibrium is involved.



The polarographic reduction waves and infrared absorption curves for $\text{Au(en)}_2\text{Br}_3$ and Au(en)(en-H)Br_2 can be interpreted satisfactorily using the structures proposed while a comparison of Au(en)(en-H)Br_2 and $\text{Pd(en)}_2\text{Br}_2$ by x-ray studies showed that the two compounds have similar crystal structures.

Because the complex compound formed between propylenediamine and chloroauric acid or potassium bromoaurate could not be isolated, a solution of potassium bromoaurate was titrated with a dilute solution of propylenediamine. Plotting the pH of the solution against the volume of diamine added gives a curve which has breaks at one, two, and three moles of diamine per mole of bromoaurate. Since the same behavior is observed with ethylenediamine, the third break is interpreted to mean that the propylenediamine complex of gold (III) loses a hydrogen in basic solutions.

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A STUDY OF SOME OF THE SALTS OF PHYTIC ACID

Peter Arvan

January 11, 1949

Phytic acid has been shown to be a hexaphosphoric acid ester of inositol (1,2). As a derivative of inositol there are eight possible geometrical isomers. Investigations have shown that phytic acid has the following stereochemical structure (3):



When sodium phytate acts as a coordinating agent, it is possible for it to complex more than one metal ion. Adjacent $(-\text{O}-\text{PO}_3)^=$ groups in the phytate group may function as bidentate and possible as polydentate units. There is some doubt, however, as to whether adjacent $(-\text{O}-\text{PO}_3)^=$ groups, which are on the same side of the plane of the ring, can function as polydentate units. The distance between two such $(-\text{O}-\text{PO}_3)^=$ groups is not much more than the distance across one carbon tetrahedron. It is doubtful, therefore, that there would be room for a metal ion to fit into a chelate structure which would form if two cis $(-\text{O}-\text{PO}_3)^=$ groups function as a unit. It seems more plausible to suppose that adjacent $(-\text{O}-\text{PO}_3)^=$ groups which are on opposite sides on the plane of the ring may form a bidentate or polydentate unit. Further, the possibility of a single $(-\text{O}-\text{PO}_3)^=$ group acting as a monodentate unit or even as a polydentate unit cannot be excluded.

The structure of the complex compounds prepared by Otolski (4) can be explained on the basis of the above theory. Otolski found that the reaction of water insoluble tetraferic phytate with various monodentate and bidentate amines gave water soluble compounds which correspond to the general formulas $\text{Fe}_4(\text{C}_6\text{H}_6\text{O}_{24}\text{P}_6)^{-6\text{MD}}$ and $\text{Fe}_4(\text{C}_6\text{H}_6\text{O}_{24}\text{P}_6)^{-4\text{BD}}$, where MD and BD represent the mono- and bidentate amines, respectively. In each case the amine used is not capable of complexing the ferric ion by itself; because of its basic nature in aqueous solution, it precipitates ferric hydroxide.

Logical formulas for these compounds can be written by assuming that two of the ferric ions are each coordinated to two $(-\text{O}-\text{PO}_3)^=$ groups. Each $(-\text{O}-\text{PO}_3)^=$ group must function as a tridentate unit in order that the coordination number of the ferric ion be satisfied. The two remaining ferric ions are each coordinated to one $(-\text{O}-\text{PO}_3)^=$ group, which functions as either a bidentate or tridentate unit; the remaining coordination positions are satisfied by three monodentate amine molecules, or by two bidentate amine molecules.

A study of the cobaltous phytate complexes has shown that the phytate group can coordinate up to four cobaltous ions. The stability of these complexes is directly dependent on the pH of the medium in which they exist. The complexes in which the cobalt to phytate ratio is 4:1, 2:1, or 3:2 were found to decompose as the pH of the solution was lowered, decomposition beginning at 8.8, 9.3, and 8.1, respectively. The products formed on decomposition are cobaltous hydroxide and a mixture of the pentacobaltous and hexacobaltous phytate. When solutions in which the cobalt to phytate ratio is 1:1 or less, are used, they do not yield the above mentioned precipitate. The only observable change is the fading of the lavender color of the complex to the pink of the hydrated cobaltous ion.

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It was concluded that the 1:1 complex is the only complex which is stable in solutions the pH of which is below seven. The experimental evidence further indicates that this complex decomposes to the hydrated cobaltous ion and the phytate group $C_8H_8O_{24}P_6H_z$ ($z=12$) where z is eight, when the pH of the solution is lowered to five.

When the cobaltous phytate complexes are titrated with sodium hydroxide, the color of the solution changes from lavender to blue, if the blue color was not present at the outset as in the solutions in which the cobalt to phytate ratio is 2:1 or greater. When the pH of the system reaches 11.5, the solutions become cloudy, and cobaltous hydroxide slowly begins to precipitate.

The cupric phytate complexes were studied polarographically (5), and a 1:1 complex was found to exist at the concentrations used. The half-wave potentials were measured in solutions which were 0.01 molar and 0.10 molar with respect to sodium phytate. In each case the cupric ion concentration was maintained constant at 5×10^{-4} molar. This study has shown that the reaction at the dropping mercury electrode is reversible, and the 1:1 complex is reduced to metallic copper (amalgam) without the intermediate formation of a cuprous complex. The half-wave potential in 0.10 molar sodium phytate solution was found to be -0.207 volts as compared to +0.016 volts for the hydrated cupric ion in 0.10 molar potassium nitrate solution (6). The dissociation constant of the complex was found to be 2.8×10^{-8} . This complex is much less stable than the bis-ethylenediamine cupric complex, which has a dissociation constant of 2.1×10^{-20} (6).

Only limited titration studies of the cupric phytate complexes were possible due to the extreme insolubility of cupric hydroxide. This study has shown that the 1:1 complex is less stable towards acid than the corresponding cobaltous complex. As in the case of the cobaltous complexes, the insoluble metal hydroxide was formed when the pH of the solutions was increased to 11.5.

An attempt was made to study the zinc and cadmium complexes polarographically, but both reductions were found to be irreversible at the dropping mercury electrode. A qualitative statement, however, may be made regarding the ease of reducibility of these complex ions. The potential at which the zinc complex begins to reduce is about -1.70 volts as compared with -1.50 volts for the $(ZnO_2)^=$ in one normal sodium hydroxide, and -1.01 volts for the hydrated zinc ion in one normal potassium nitrate solution (5). The potential at which the cadmium complex begins to reduce is -0.75 volts as compared to -0.59 volts for the hydrated cadmium ion in one normal potassium nitrate solution (5).

A study of the calcium phytate complexes has shown that the 1:1 complex is the only one which can be prepared in solution. All attempts to increase the calcium to phytate ratio resulted in the formation of an insoluble material, which analysis indicated to be $Ca_2P_6 \cdot C_8H_8O_{24}P_6 \cdot 3H_2O$ (7).

On standing, solutions in which the ratio of calcium to phytate was 1:1 or less also yielded precipitates which were shown to be the dicalcium octasodium phytate trihydrate.

The evidence appears to support the theory that the calcium ion is complexed by the phytate group. No precipitate of calcium carbonate or calcium oxalate is formed if a solution which contains both calcium ion and the phytate group is treated with a solution of sodium carbonate or sodium oxalate. Solutions of calcium ion alone, with the pH adjusted to the same value as in the case in which phytate is used, give immediate precipitates with sodium carbonate or sodium oxalate.

This study has shown that the phytate group is an excellent complexing agent in basic solution. Under the proper conditions, it may complex unusually large amounts of metal ions, as demonstrated in the case of the cobaltous ion. Some preliminary tests have shown that this material may be of value as a sequestering agent to be used in metal plating baths.

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The Nature and Determination of Hydrogen Bonding

Milton Tamres

February 15, 1949

History:

It had been recognized for many years that the anomalous behavior of certain molecules could best be interpreted by assuming "complex" compound formation. Abnormal molecular weights from freezing point determinations, deviations from Raoult's Law², the weakness of ammonium hydroxide as an electrolyte compared with tetramethylammonium hydroxide³, the activity of alpha hydroxy-anthraquinone as compared with the beta isomer⁴, etc., were explained on the basis of molecular association. Indeed, Nernst⁵ was quite successful in accounting for the distribution of benzoic acid between water and benzene by assuming double molecules in the benzene phase. However, these observations remained unrelated until 1920 when Latimer and Rhoadbush⁶ proposed the concept of hydrogen bonding and indicated the importance and widespread occurrence of the hydrogen bond.

Nature:

Latimer and Rhoadbush assumed that a proton attached to one atom by a covalent linkage could be attracted to a pair of electrons on another atom to form a second covalent bond, i.e.,

$\text{H} \quad \text{H} \cdot$ This structure is in violation of the Pauli exclusion principle, unless it is assumed that the outer orbitals of hydrogen are partaking of bond formation. Pauling^{7,8} states that the bond-forming power of the outer orbitals of the hydrogen atoms is negligibly small, and concludes that the hydrogen bond is essentially an electrostatic attraction between unshielded electrons on one atom and a proton attached to another atom. This proposal is in accord with the experimental observation that the strength of the hydrogen bond appears to increase both with the electronegativity of the atom directly bonded to the hydrogen and the electronegativity of the next nearest atom to which the hydrogen is also bound, apparently more weakly.

The correlation of the strength of H bonds with electronegativity appears to break down when the H bond forming capacity of nitrogen and of chlorine are compared. Although they have approximately the same electronegativity, chlorine forms much weaker H bonds than does nitrogen. This may be attributed to the large size of chlorine, as compared with nitrogen, which causes its electrostatic interactions to be weaker than those of nitrogen⁸.

The hydrogen bond has also been described as an electrostatic interaction of an array of dipoles. Hildebrand^{9,10} has clearly shown, however, that dipole attraction alone is insufficient to displace the hydrogen bond concept. For example, phenol is much more soluble in water than it is in nitrobenzene, although the latter has a much higher dipole moment.

Evidence for Hydrogen Bond Formation:

Before discussing the evidence for hydrogen bonding, it is necessary to distinguish among the different types of H-bonds. These may be classified as follows:

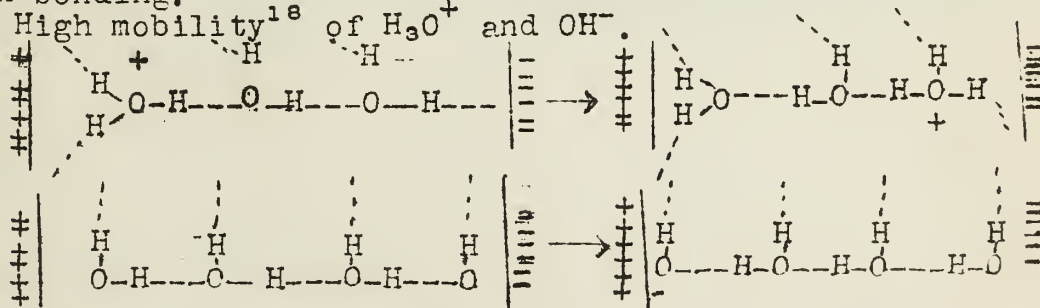
Type A: intermolecular H-bonds between like molecules, i.e. $(\text{H}_2\text{O})_x$ or $(\text{CH}_3\text{COOH})_2$, each molecule containing both a hydrogen capable of bonding and an atom with an exposed pair of electrons.

Type B: intermolecular H-bonds between unlike molecules, i.e., chloroform-acetone or chloroform-pyridine, one molecule containing a hydrogen atom capable of bonding and the other molecule containing the atom with an exposed electron pair. Each behaves normally in the absence of the other.

Type C: intermolecular association or chelation, i.e., o-hydroxybenzoic acid. This type of bonding is most stable when the chelate forms a six-membered ring. It is less stable for a five-membered ring and is far less stable for a seven-membered ring.

In general, type A will exhibit the following abnormalities.

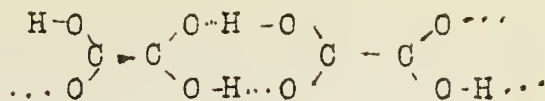
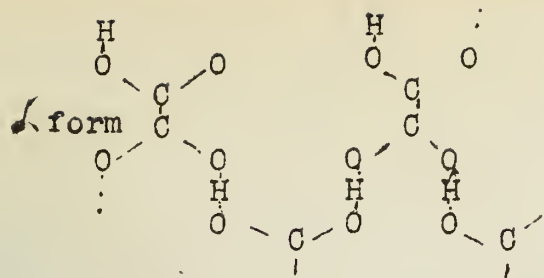
1. Abnormally high molecular weights, i.e. alcohols, acids, oximes, etc. The average molecular weight increases with an increase in concentration and with a decrease in temperature.
2. Abnormal dielectric constant. The square root of the dielectric constant will not be proportional to the dipole moment¹¹. This deviation may be positive as for $(\text{HF})_x$ ¹² and $(\text{H}_2\text{O})_x$, or may be negative as for fatty acid dimers.
3. Deviations from Raoult's Law, i.e., high solubility of phenol in water.
4. Association of liquids, i.e. $(\text{H}_2\text{O})_x$, $(\text{HCN})_x$, $(\text{HF})_x$, the degree of association decreasing with an increase in temperature. These liquids have high heats of vaporization, high melting points and boiling points, high specific heats and abnormal vapor pressures.
5. Molar refraction studies¹³. Hydrogen bonding solvents affect the molar refraction of molecules having electron releasing and electron attracting groups at the end of conjugated chains, i.e., $\text{R}_2\text{N}^+ = \text{C}_6\text{H}_4 = \text{CHO}^-$.
6. Dimerization of fatty acids in non-polar solvents and in the vapor state.
7. Shift in the characteristic absorption band of the X-H group as determined from Raman¹⁴ and infrared studies¹⁵. The intensity of the shifted band depends upon the concentration¹⁶ and the temperature¹⁷, i.e., upon the extent of H-bonding.
8. (a) High mobility¹⁸ of H_3O^+ and OH^- .



The fact that the ammonium ion has a much lower conductance in liquid ammonia than does the hydronium ion in water indicates that ammonia is far less associated. ¹⁹

(b) Maximum density of water at 4°C.

9. Unusual physical properties of crystals, i.e., low density of ice, alpha and beta oxalic acid.



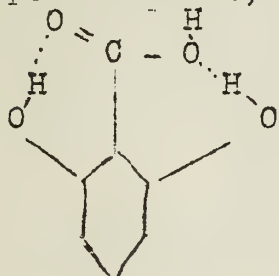
B form

The type B hydrogen bond will effect the same abnormalities as the type A bond. Hence, the methods used in detecting the latter may also be employed for the former, i.e., dielectric constant²⁰, Raman and infrared spectra, etc. There are several methods, worth mentioning, which are particularly useful in studying the type B bond since simple "addition compounds" are formed in this case.

1. Cryoscopic measurements²¹. A plot of temperature as a function of percentage composition yields the composition of the complex, i.e., o-chlorophenol-pyridine.
2. Measurement of deviations from Raoult's Law²²; solubilities²³, vapor pressures, viscosities²⁴, densities²⁵, heats of mixing²⁶⁻³⁰, etc. Excluding solubility measurements, a plot of the deviation from Raoult's Law as a function of the percentage composition gives the composition of the complex (from the point of maximum deviation).
3. Determination of equilibrium constant³¹ of the complex from freezing point lowering, i.e., o-chlorophenol + pyridine in benzene.

An atom which takes part in the formation of one H-bond has no tendency to partake of another. Consequently, molecules of type C, the chelates, exhibit normal behavior. Chelation may be inferred from the following effects.

1. Shift of the characteristic vibrational bond of the X-H group as determined from Raman and infrared spectra. In this case, there is no shift upon dilution towards the normal X-H vibrational frequency.
2. Differences in conductivity and acid strength of certain ortho substituted phenols as compared with the meta and para isomers, i.e., 2,6 dihydroxy benzoic acid⁹ is a strong acid, stronger than phosphoric and sulfurous acid, its acid constant having the value 5×10^{-2} .



The Position of the Hydrogen Atom

The poor scattering properties of the hydrogen atom make the methods of X-ray and electron diffraction unsuitable for determining the position of a hydrogen atom in a molecule. It is very likely that direct evidence of its position will be forthcoming from neutron diffraction studies, since the hydrogen nucleus has a large cross-section for neutron scattering.

Several indirect methods have been employed. In the structure A-H---B, the influence of B on the A-H interatomic distance may be calculated from the resulting shift of the characteristic vibrational frequency of the A-H group³². The fact that the absorption frequency of the O-H group in water vapor is altered

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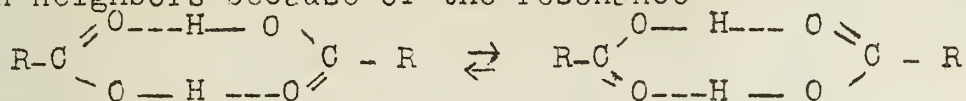


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only slightly in water and ice indicates that the O-H interatomic distance in the liquid and the solid cannot be appreciably different from that in the vapor³³. In the gas molecule the O-H distance is 0.96\AA . The distance between neighboring oxygen atoms in ice is 2.76\AA , as determined by X-ray investigation. It is clear, then, that in ice the position of the hydrogen atom in O-H---O is unsymmetrical with respect to its two oxygen neighbors. Pauling has shown that this proposed structure for the ice crystal is in agreement with the observed residual entropy of ice.^{34,35}

It may be suspected that the hydrogen atom in fatty acid dimers may be symmetrically located with respect to its two oxygen neighbors because of the resonance



However, the X-ray study of Karle and Brockway shows that the structure must be an unsymmetrical one since the C-O and C=O distances are not equivalent³⁶.

In certain crystals of oxygen and fluorine compounds, i.e., KH_2PO_4 and KHF_2 , unusually short interatomic distances are observed³⁷. In KH_2PO_4 , for example, it is inferred that a hydrogen atom must be between two oxygen atoms to account for the short O-O distance of 2.55\AA .

The Strength of the Hydrogen Bond.

The strength of the H-bond in A-H---B increases with an increase in electronegativity of the A or B atom. Thus, it is found in general that fluorine forms especially strong H-bonds and nitrogen and oxygen form slightly weaker bonds. The bond strengths range in value from approximately 3-8 k.cal. per mole per bond. Much weaker bonds are formed by chlorine, bromine, carbon and sulfur. Mercaptans show no evidence of hydrogen bonding whereas thiophenols do, as would be expected from the increase in electronegativity of A.

Numerous methods have been employed to calculate the strength of H-bonds, and a few will be mentioned.

1. The shift in frequency of the characteristic vibration of the A-H group is a measure of the strength of the H---B bond.
2. From the heat of sublimation of $(\text{HF})_x$, the strength of the H-bond is calculated to be 6.7 k.cal./mole.³⁸
3. The energy of the H-bond in fatty acid dimers³⁹ has been obtained by determining the equilibrium constant of the vapor at two temperatures and calculating H from the equation $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$
4. Determination of the equilibrium constant at two temperatures for the system o-chlorophenol + pyridine (using benzene and p-dichlorobenzene as the solvent at the lower and higher temperature respectively) gives a value of 6.8 k.cal./mole for the strength of the bond³⁹.

When a hydrogen bond is formed the strength of the A-H linkage in A-H---B is weakened. Similarly, when a hydrogen bond is broken the A-H bond becomes stronger. Thus, the experimental value of the strength of H-bonds is only a partial measure of the actual strength⁴⁰.

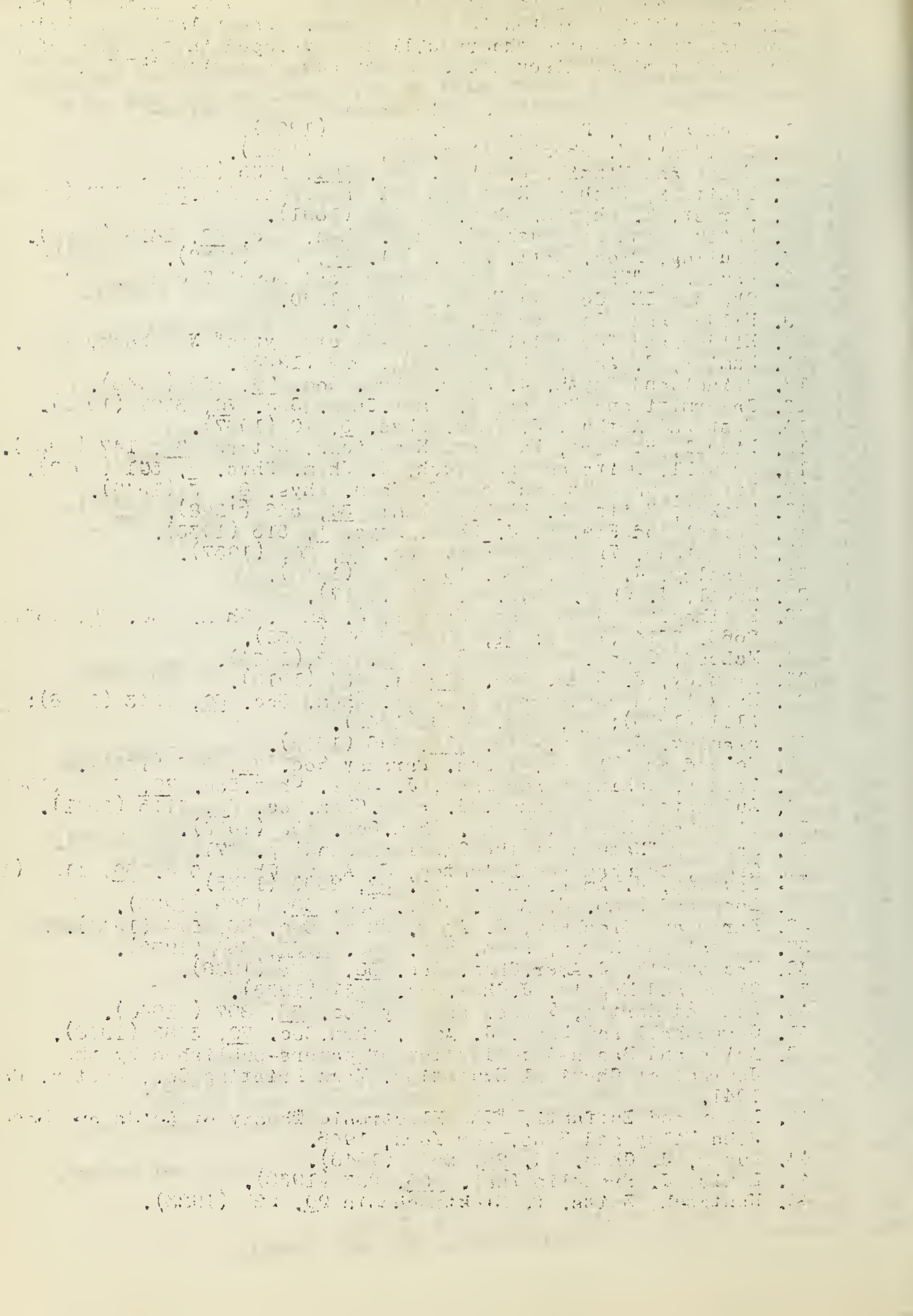
Although hydrogen bonding alone may explain a large number of observations, it is frequently not possible to eliminate other forces, i.e., dipole attraction, steric hindrance⁴¹, etc. Therefore, it is always best to consider hydrogen bonding as an important contributing factor.

Relation of H-Bonding to Acid-Base-Theory.

A number of investigators have expressed the view that hydrogen bonding is an intermediate step in neutralization reactions in which a proton is transferred. The relation of hydrogen bonding to acid-base theory will be developed in the form of an informal seminar discussion. References are given⁴¹---

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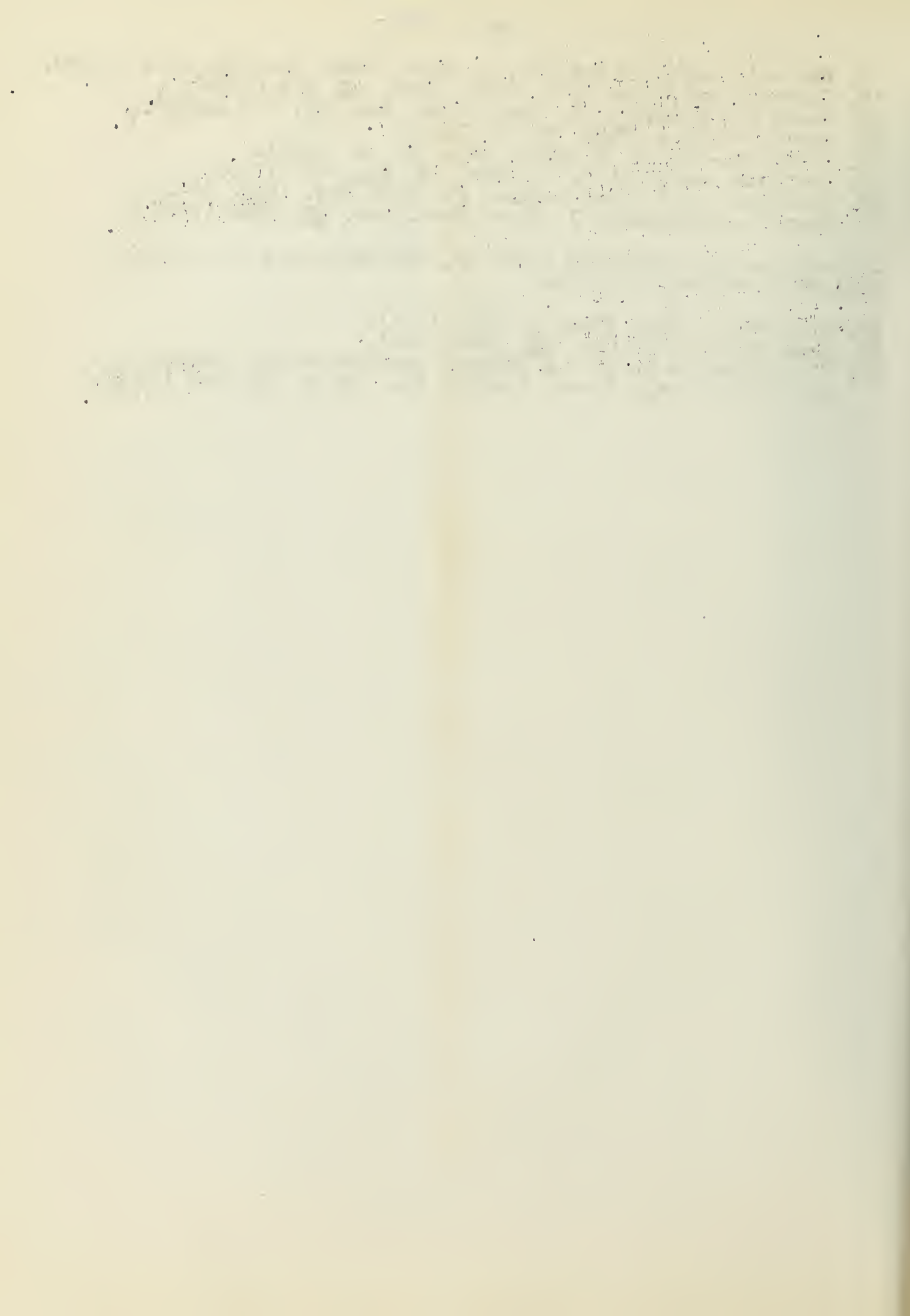
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Heats of Adsorption of Water Vapor on Hydrous Oxides

Gordon L. Bushey

22 February 1949

Introduction. Phenomena associated with physical and chemical adsorption of gases and vapors on solid adsorbents have intrigued numerous investigators in the past half century.¹⁻⁴ The term physical adsorption is most often used to describe surface condensation due to various forces grouped together as vander Waals force while chemisorption is regarded as surface reaction involving electrovalence or covalence forces. An example of borderline cases is the ion-permanent dipole interaction which can be regarded as either the upper limit of van der Waals forces or the lower limit of chemical forces.¹ In this intermediate zone falls the adsorption of water vapor on the highly developed surfaces of hydrous oxides. Laws dealing with equilibrium states only, without involving any sort of mechanism, are equally valid for both adsorptions; thus from simple thermodynamics the heat change involved in adsorption may be calculated utilizing the Clausius-Clapeyron equation:

$$(1) \quad \frac{d \ln P}{d (1/T)} = - \frac{q}{R} \quad \text{where all terms have their usual meaning.}$$

Physical Nature of Adsorption Forces. According to modern theory the interaction forces between surfaces and molecules or atoms may be classified as repulsive electrostatic forces and attractive van der Waals forces, the latter of three types: (a) orientation-Keesom, (b) induction-Debye, and (c) dispersion - London. The orientation and induction forces arise from the interaction of permanent dipoles and vary as r^{-7} . Since the torques of rotating dipoles tend to keep the dipoles in oriented or parallel positions these positions of lower potential energy will be statistically predominant resulting in a net attraction. Moreover, for polarizable dipoles there is an induced dipole interaction (or induced quadrupole term). The possibility of fluctuating dipoles because of electronic motion is the basis of London's so-called dispersion forces, which cause an attraction between non-polar atoms or molecules, also varying as r^{-7} .

On the basis of these forces, the interaction potential has been calculated for various idealized cases: (a) dipole molecule and polarizable (conducting) surface, (b) polarizable dipole and conducting surface, (c) non-polar-molecule and electric charges causing induced dipole, (d) and a fluctuating dipole on conducting surface or (e) electric charges.⁵⁻⁷ These interaction potentials have been found to vary as r^{-3} .

In the process of building up an adsorbed layer on the surface a summation of these forces operates, the adsorbate-adsorbate interaction being negligible at first but assuming increased importance with the development of a continuous adsorbed phase.⁸⁻¹¹ When a liquid surface is present, the surface tension is the physical manifestation of these interactions so that changes in extent of surface involve these heat effects, particularly in capillary condensation and desorption isotherms.^{12,14}

Experimental and theoretical heats of adsorption assuming various models of the adsorbed material are proving useful in determining the physical state of the adsorbate and predicting adsorption characteristics of mixtures of fases.^{13,14}

III. Isothermal Adsorption Equations. Besides the purely empirical Freundlich isotherm: $v = kp \frac{1}{n}$ where v = vol. adsorbed at pressure p and k, n = arbitrary constants, several statistical, thermodynamic, and kinetic treatments have found wide application. In 1938 Brunauer, Emmett, and Teller¹⁵ proposed an extension for multi-layer adsorption of the inadequate Langmuir monomolecular concept:

$$(2) \text{ Langmuir: } \frac{P}{V} = \frac{1}{V_{mb}} + \frac{P}{V_m}$$

$$(3) \text{ B.E.T. } \frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{P}{P_0}$$

where: P_0 = vapor pressure of adsorbate at saturation
 V_m = volume of vapor corresponding to a monolayer
 C = constant proportional to $\exp. (E_1 - E_L) / RT$
 E_1 = average heat of adsorption for the first layer
 E_L = heat of liquefaction of adsorbate

The latter equation is widely used in calculating surface areas of finely divided solids with adsorbates of known molecular or atomic dimensions. From the density d of the liquid (or solid), Avogadro's number N , and the molecular weight M , the cross-sectional areas of various gas molecules are obtained by means of the equation:

$$(4) \text{ Cross-sectional area} = 4 \times 0.866 (M / 4 \times 2 N_d)^{2/3}$$

Another adsorption isotherm developed by Harkins and Jura¹⁶ and extended by Gregg²² and Ross²¹ from considerations of similarities between adsorption pressures and surface pressures of films on liquids and solids.²⁴

$$(5) \text{ Harkins-Jura: } \ln P/P_0 = B - A/V^2$$

$$\Sigma = KS^{1/2}$$

where: A, B , and k are constants depending upon the system

S = slope of straight line plot of equation (5)

Σ = specific surface of the solid

Literature of the past ten years is voluminous with applications and comparisons of equations (3) and (5), as well as criticism and modification. Variations in experimental heats of adsorption with amount adsorbed has influenced some of these revisions, including the dual-surface concept^{18,23}, coordination factors²⁰, and extension of the force field of the adsorbent beyond one molecular diameter of adsorbate.^{17,19,25}

Information on the structure of porous adsorbents may be gleaned from sorption-desorption isotherms^{26,27} by careful application of the Kelvin equation for the change in vapor pressure with curvature of a liquid surface.

$$(6) \ln P/P_0 = - \frac{2 \gamma}{r} \frac{M}{dRT} \cos \theta$$

where: γ = surface tension

r = radius of capillary

θ = angle of wetting

IV. Experimental Determination of Heats of Adsorption. Two methods are available for the experimental measurement of heats of adsorption: (a) the direct or calorimetric method, and (b) the indirect or isosteric method. Recent refinements in calorimetric technique made by Beebe³⁷ and his coworkers permit the accurate detection of variations in the differential heat of adsorption which are smaller than the experimental error involved in earlier work in this field. Integral heat of adsorption and heat of wetting have commonly been determined calorimetrically. The isosteric (or less correctly, isothermal) heat of adsorption always refers to a definite quantity of gas adsorbed at different temperatures and pressures, and may be calculated from the slope of a straight line plot of equation (1) or from the integrated form for a small pressure and temperature range:

$$(7) q \text{ isosteric} = \frac{RT_1 T_2}{T_1 - T_2} \ln \frac{P_1}{P_2}$$

A method of estimating the average heat of adsorption in the first layer is implied in the equation (3) of Brunauer, Emmett, and Teller.

Data for the calorimetric and isosteric heats of adsorption of water vapor are limited. Coolidge²⁸, Keyes, and Marshall²⁹ report that both heats on charcoal start with low values at small adsorption and increase with further adsorption. Coolidge also indicate a heat of adsorption of smaller magnitude than the heat of condensation of water at all temperatures above 10°C. The heat of wetting, a measure of the difference between integral heat of adsorption and heat of liquefaction, has been measured by Patrick and Grieder³⁰ and Culbertson and Winter³¹ for silica gel. Of particular interest are the isosteric heats of adsorption of water on some crystalline amino acids³² where evidence is presented that at low pressures one water molecule per polar group or peptide linkage corresponds to a B.E.T. monolayer. This is at variance with the idea advanced by Pauling³⁹ that adsorption of water on peptide linkages of proteins is inappreciable.

Heats of adsorption of adsorbates other than water have been investigated extensively, and reviews have appeared in the literature.^{34,38} For the adsorption of halogens on silica gel Reyer³⁵ and coworkers have found that the net heat of adsorption $[(E_1 - E_L)]$ of BET equation (3) is positive for chlorine, about zero for bromine, and negative for iodine. Quite recently Joyner and Emmett⁴⁰ have calculated the isosteric heats of adsorption of nitrogen on carbon blacks for which accurate and unusual calorimetric heats had been previously measured.³⁷

Experimental Results of Present Investigations

[To be presented before the Division of Colloid Chemistry, 115th A.C.S. Meeting, San Francisco, March 30, 1949]

A. Hydrous oxides examined Surface Area M²/G (20° ave.)

1. Standard SiO ₂	405
2. γ-Al ₂ O ₃ ·H ₂ O ² (ex SO ₄ , 25°C.)	1040
3. TiO ₂ (pptd. at 0°C.)	900
4. SnO ₂ (pptd. at 100°C.)	320
5. ZrO ₂ (ex Cl ⁻ , 0°, 8.5 pH)	945
6. ZrO ₂ (ex NO ₃ , 30°, 4.5 pH)	1220

B. Variation of net heats of adsorption with amount adsorbed

C. Aging effect on zirconia

D. Changes in free energy and entropy for the process: H₂O(liquid) → H₂O(adsorbed) 1. $\Delta F = RT \ln P/P_0$ 2. $T\Delta S = \Delta H - \Delta F$

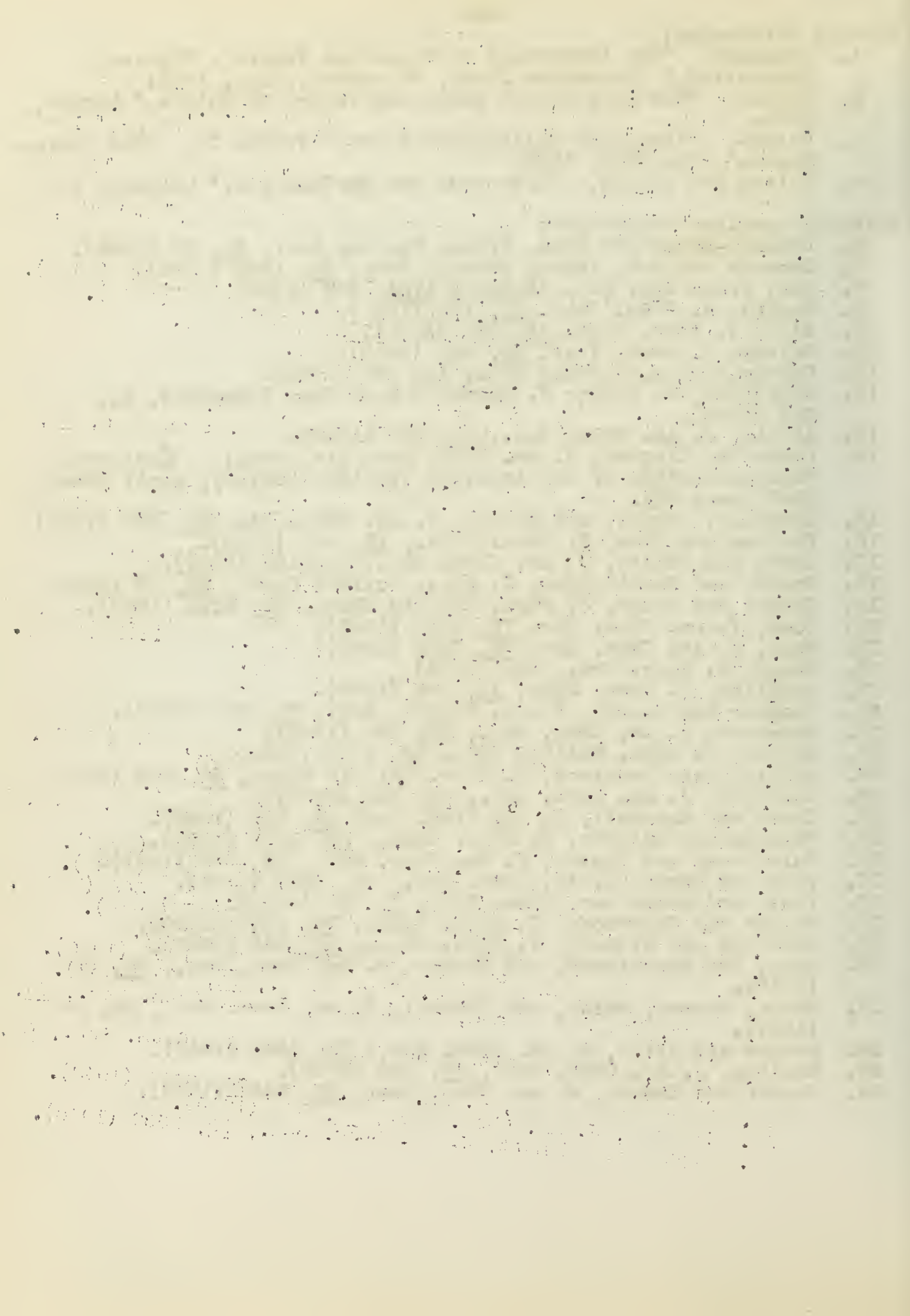
E. Additional calculations possible and further investigations indicated.

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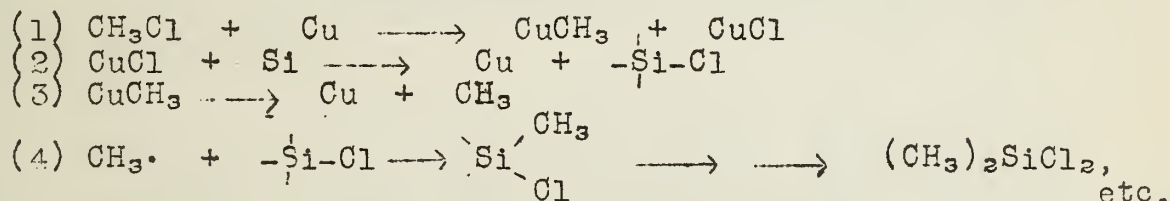
RECENT STUDIES IN ORGANOSILICON COMPOUNDS

Scott Searles

March 1, 1949

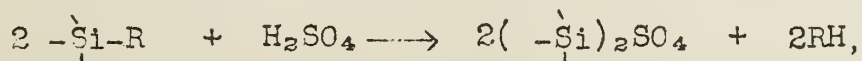
Organosilicon chemistry continues as a very active field of research and since the last reviews^{1,2} covering the published work to June, 1946, the knowledge of this subject has been considerably extended. The research now appears to center on the effect of a silicon atom on the reactivity of adjacent groups and on the discovery and investigation of new reactions and new types of compounds. Although certain analogies to carbon chemistry are still useful, the chemical behavior of silicon is now recognized to resemble that of germanium and boron much more than that of carbon. Silicon is much more electropositive in nature than carbon, and furthermore, the unused 3d-orbitals in its outer shell permit it to attain a covalency of 6 in favorable cases. This factor opens up an entirely new reaction mechanism for silicon compounds, which is not available in the carbon series.

Syntheses. The classical methods, involving the reaction of a silicon halide with an organo-metallic compound, such as dialkylzinc, diarylmercury, arylsodium or the Grignard reagent, are still used, particularly the Grignard method^{3,4}. The extension of this general reaction to the use of organolithium compounds, introduced relatively recently by Gilman, has become the method of choice for many preparations^{5,6}. Direct synthesis from alkyl halides and elementary silicon at about 300° with powdered copper as a catalyst is of great interest⁷. The mechanism for the methyl chloride reaction has been studied and deduced to follow the following sequence:



The peroxide-catalyzed addition of trichlorosilane to olefins and acetylenes proceeds smoothly in the same manner as the analogous reaction with chloroform, and is a method of choice for the preparation of many alkyltrichlorosilanes⁸.

Properties and Reactions of Organosilicon Compounds. A very high degree of stability of the C-Si bond characterizes the tetraalkylsilanes and the tetraarylsilanes, which are actually less susceptible to various reagents and to pyrolysis than their carbon analogs¹. The reactions which these compounds undergo are mainly those typical of the organic groups, such as chlorination of the alkyl groups, and nitration or sulfonation of the aromatic groups. In aromatic substitution, however, silyl groups show peculiar orienting effects which are sometimes the reverse of the analogous carbon groups⁷. The C-Si linkage is cleaved by aluminum chloride, however, and by hot, concentrated H₂SO₄,



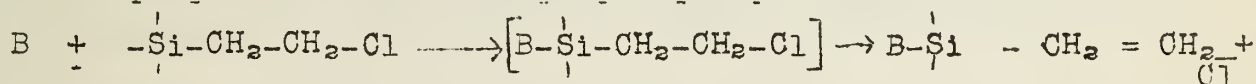
the latter forming the basis of a recently proposed method for the qualitative identification of organosilicon compounds⁹. The C-Si bond is much less stable in unsymmetrical tetrasubstituted

silanes, such as in the readily hydrolyzable phenyltriethylsilane, and the higher silanes with Si-Si bonds are also less stable, due to the ease of hydrolysis of the Si-Si bond.

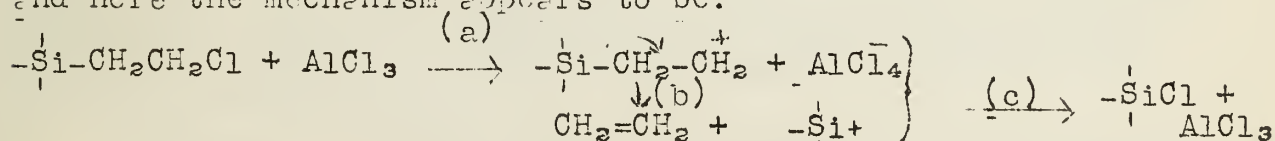
The α - and β -halogen derivatives of the tetraalkylsilanes and the trialkylchlorosilanes possess some very interesting properties. A β -halogen is exceedingly reactive towards silver nitrate and a great variety of bases, while an α -halogen is relatively inactive. The α -chlorine in chloromethyltrimethylsilane is less reactive than the halogen in *n*-hexyl chloride but considerably more active with respect to replacement by hydroxide or iodide (S_N2 mechanism) than the chlorine in its notoriously inactive analog, neopentyl chloride, suggesting that the silanes are less sterically hindered. On the other hand, both the chloromethyl and iodomethylsilane are practically inert to silver ion (S_N1 mechanism) which does react with neopentyl chloride. Whitmore's explanation¹⁰ that this is caused by the electronegativity of silicon compared with carbon does not seem acceptable; perhaps the inability of the silylmethyl carbonium ion to stabilize itself by rearrangement as the neopentyl carbonium ion does, may be a factor.

Further chlorination of a chloromethyl silane (R_3SiCH_2Cl) gives a dichloromethylsilane ($R_3SiCHCl_2$), a chloromethyl group being chlorinated in preference to a methyl group¹¹. While monochloromethylsilanes react with alkalis to give typical alcohols¹² the dichloromethyl compounds are cleaved by alkali at the C-Si bond to give methylene chloride. Trichloromethylsilanes are cleaved very readily to form chloroform¹³. The ease of cleavage of the Si-C bond increases with degree of chlorination of the particular carbon atom involved, and each chloromethyl group seems to act independently¹⁴.

A β -chlorine is very easily removed by a wide variety of reagent, including cold, dilute aqueous sodium hydroxide, but instead of simple replacement of the chlorine, the side chain is cleaved from the silicon atom, forming an olefin. This has been termed " β -elimination". The experimental facts are consistent with the following mechanism¹⁵:



The β -halogen also reacts readily with acidic reagents such as silver ion and aluminum chloride, with formation of an olefin, and here the mechanism appears to be:

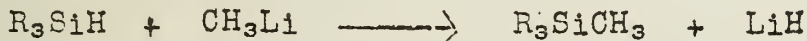


The presence of an ethylenic bond adjacent to a β -chlorine greatly deactivates the latter, as might be expected from the similar effect in organic compounds. A compound with this structure has been prepared recently by Agre¹⁶, in an interesting manner. Trichlorosilane does not add to trichloroethylene under the usual conditions for addition to olefins, because this double bond is not sufficiently active, but at 500° this olefin dehydrochlorinated forming dichloroacetylene, to which the trichlorosilane then added in 87.5% overall yield.

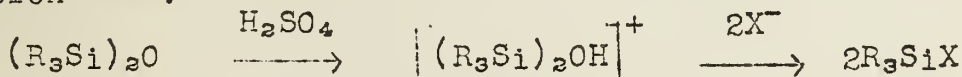
The instability of organosilicon compounds having oxygen attached to a β -carbon is closely related to " β -elimination" Attempts^{17,18} to prepare such compounds, as by causing trimethylsilylmethylmagnesium chloride to react with acetyl chloride, carbon dioxide or phenyl isocyanate, generally yield only decomposition products that apparently result from Si-C cleavage of the expected product. The explanation was that this instability is due to the positive nature of the β -carbonyl carbon. The reaction of the above magnesium compound with ethyl chloroformate to form a 75% yield of the rather stable ethyltrimethylsilylacetate, however, has been announced recently. This substance undergoes the expected Si-C cleavage, when treated with acids or bases, and the previously mentioned mechanism for " β -elimination" appears to apply.

Allyltrimethylsilane is an interesting new compound²⁰. It adds hydrogen and chlorine normally across the double bond and, at low temperatures, bromine and hydrogen halides also; but above 40° acids and bromine cause cleavage of the allyl group, presumably via an unstable β -carbonium ion. Treatment with alkali has a similar result, with the relatively stable allyl anion being replaced by OCH_3^- , for instance, much as in the hydrolysis of a chlorosilane.

Trialkyl- and triarylsilanes resemble the tetra-substituted compounds, except that the Si-H bond is easily cleaved by aqueous alkali with formation of hydrogen gas. A study of this reaction by Price²¹ indicates that it proceeds by a nucleophilic attack of hydroxide on the silicon atom, causing release of a hydride ion, which reacts with a proton from the solvent to form H_2 . The hydrogen of trialkyl- and triarylsilanes can be replaced (by probably a similar mechanism) directly by an alkyl group by means of alkyllithium compounds²²:



The trialkyl- and triarylchlorosilanes are well known, as they are common reaction products from the Grignard synthesis. They, as well as the corresponding fluorides and bromides, also may be prepared from the related siloxane by means of the Flood reaction^{23,24}:



Other methods are also available for the fluorides, which are being given commercial attention now because of their great stability. Iodides are best prepared by the cleavage of an Si-C₆H₅ bond with iodine.

In general, a halogen attached to silicon is very reactive toward basic reagents, although the activity decreases with increasing size of the alkyl groups on silicon²⁵. Hydrolysis occurs readily in the presence of water²⁶, usually to form the siloxane, but under carefully controlled alkaline conditions the corresponding silanol may be obtained²⁷. Trialkylsilanols are very interesting because they are much stronger acids than alcohols. With ammonia trialkylchlorosilanes react to form either trialkylamino-silanes or hexaalkyldisilazane $(\text{R}_3\text{Si})_2\text{NH}$, depending on the reaction conditions. The amino compounds are not at all like the organic amines, for they react readily with hydrogen halides to form the trialkylhalosilane and ammonium chloride²⁸.

A great many dialkyl- and diaryldihalosilanes are known, as they are readily prepared by the Grignard reaction or the direct synthesis and are of great commercial importance as intermediates in the preparation of silicone polymers. When treated with water these compounds hydrolyze to silanediols, which usually condense to polysiloxanes or "silicones" immediately. It is interesting that a large proportion of the polymers found by the spontaneous process consist of cyclic trimers and tetramers, which are distillable liquids. Prolonged heating of the linear polymer causes rearrangement into these cyclic forms also, but by treatment with more dichlorosilane the cyclic compounds can be converted into the commercially more useful linear polymers. By use of trialkylchlorosilanes to provide inert end-groups, the length of the chains may be controlled, and by use of alkyltrichlorosilanes and vinyl groups attached to silicon any degree of cross-linking can be attained, thus making a wide variety of polymers possible⁷. When the two organic groups attached to silicon are different, there are some interesting possibilities of stereoisomerism in the cyclic trimers and tetramers; a few of these have been isolated²⁹.

The possibility of organosilicon polymers having methylene or imino groups bridging the silicon atoms appears to be under investigation at present. High molecular weight linear polysilylmethylene compounds³⁰ and polyalkylsilazanes^{31,32} were both reported recently. The silazanes show an even greater tendency to form cyclic trimers and tetramers than the polysiloxanes.

The present attention given to polymeric silicon compounds calls to mind a study of the polymethyl metasilicates made twenty years ago³³. These polyesters were prepared by a slow, controlled hydrolysis of methyl orthosilicate or of silicon tetrachloride in methanol, so that the hydroxyl groups condensed as they were formed. The polymers obtained in this way were chiefly linear of a relatively low degree of polymerization, but there was evidence from the analytical data that ring formation became increasingly important with increasing polymer size.

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Recent Developments in the Radioactive Transformation Series Among the Heavy Nuclei

Eugene P. Bertin

8 March 1949

The progress that has been made in the field of radioactivity largely as a direct or indirect result of the Manhattan project and of the development of the chain-reacting pile and the 184-inch cyclotron, is reflected in the growth in the number of known isotopes. G. T. Seaborg's table of isotopes when first published in 1940 listed 332 artificially radioactive isotopes, the first revision (1944) 425, and the latest revision (1948) over 700 (9). Possibly in no part of the periodic table is this progress more evident than among the heavy nuclei. Before discussing the advances that have been made in this field, however, a brief review of radioactivity in general is in order.

I. Causes of Nuclear Instability

Radioactivity may be defined as the collective phenomena attendant upon the transitions of atomic nuclei from unstable to stable states. A nucleus may be unstable for any of 3 general reasons:

1. Sheer Mass---No stable nuclei of atomic number (Z) greater than 83 (Bi) exist.
2. Incorrect Neutron:Proton Ratio (N:Z)---Fig. 1 shows the curve of most stable N:Z ratios; N:Z is 1:1 for nuclei of Z less than 20 (Ca) and steadily rises to a value of 1.6:1 for Z = 92 (U). The following table of selected nuclei illustrates this increase:

Nucleus	% Abund.	N	Z	N:Z
$^{10}\text{Ne}^{20}$	90	10	10	1.00
$^{20}\text{Ca}^{40}$	97	20	20	1.00
$^{33}\text{As}^{75}$	100	42	33	1.27
$^{41}\text{Cb}^{93}$	100	52	41	1.27
$^{53}\text{I}^{127}$	100	74	53	1.40
$^{65}\text{Tb}^{159}$	100	94	65	1.45
$^{73}\text{Te}^{181}$	100	108	73	1.48
$^{83}\text{Bi}^{209}$	100	126	83	1.52
$^{92}\text{U}^{238}$	99	146	92	1.59

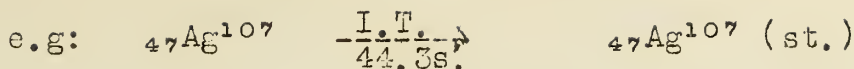
The N:Z curve retains its full significance for Z above 83 where it shows which nuclei will have the longest decay periods. Of course, nuclei wherein the N:Z ratio deviates too greatly from the ratio of greatest stability will be unstable, i.e., radioactive.

3. Adjacence to a Stable Isober---Two nuclei of the same mass number ($A = N + Z$) which differ in atomic number (Z) by 1 cannot both be stable. Only 3 exceptions to this rule are known: $^{48}\text{Cd}^{113}$ - $^{49}\text{In}^{113}$; $^{49}\text{In}^{115}$ - $^{50}\text{Sn}^{115}$; $^{51}\text{Sb}^{123}$ - $^{52}\text{Te}^{123}$.

II. Radioactive Decay Processes

Nuclear instability may be rectified by the following processes (See Figs. 1 and 2.)

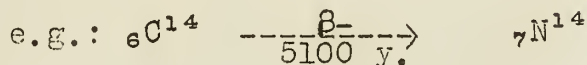
1. Internal transition---In some cases a mere rearrangement of the nucleus or adjustment of the energy state therein, perhaps accompanied by the emission of a γ -photon, suffices to stabilize the nucleus. Such transformations are known as "internal transitions" and the nuclei as "isomers"



There are cases of twin isomers, both unstable (e.g., Ca^{49}), and of 3 isomers, all instable (e.g., Sb^{124}).

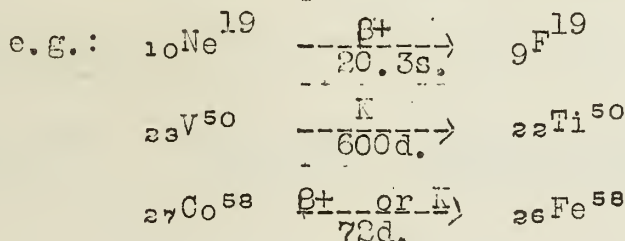
2. Adjustment of the N:Z ratio---

a. N:Z too large---Emission of a β -particle (electron) with consequent conversion of a neutron to a proton.



b. N:Z too small---In this case, one of the protons can be converted into a neutron by one or the other or both of 2 processes:

- (1) Emission of a positron (β^+)
- (2) Capture of a satellite (usually K) electron.
This is known as "K-electron capture".



3. Adjustment of mass---The heavy nuclei must lose mass as well as charge. This is efficiently accomplished by the emission of α -particles ($_{2}\text{He}^4$ nuclei) whereby 4 units of mass and 2 of charge are lost at once. One might expect that by a series of such emissions the mass of, e.g., U^{238} , could be brought into a stable configuration below $Z=83$, and indeed, U^{238} , as well as U^{235} and Th^{232} are parents of long "transformation series" of, chiefly, α -disintegrations. However, the α -decay does not quite follow the N:Z-curve of greatest stability (see Fig. 1) so that an occasional β -emission is necessary to adjust this defect before further α -decay can proceed.

III. Natural and Artificial Radioactivity

1. Natural radioactivity---Two groups of nuclei fall into this category:

- a. All nuclei of Z greater than 83 (Bi).
- b. The following nuclei of lower Z:

Nucleus	% Abund.	Half Life	Decay	Mev.	Product
$_{19}\text{K}^{40}$	0.012	$2.4 \times 10^8 \text{ y.}$	β^- $\beta^+, \text{ K}$	1.3	$_{20}\text{Ca}^{40}$ $_{18}\text{Ar}^{40}$
$_{37}\text{Rb}^{87}$	27.2	$6.3 \times 10^{10} \text{ y.}$	β^- γ	1.5 0.13	$_{38}\text{Sr}^{87}$
$_{62}\text{Sm}^{148}$	11.27	$1.4 \times 10^{11} \text{ y.}$	α	2.0	$_{60}\text{Nd}^{144}$
$_{71}\text{Lu}^{176}$	2.5	$2.4 \times 10^{10} \text{ y.}$	β^- K	0.4	$_{72}\text{Hf}^{176}$ $_{70}\text{Yb}^{176}$
$_{75}\text{Re}^{187}$ $_{60}\text{Nd}^{150?}$	61.8 5.95	$3. \times 10^{12} \text{ y.}$	β^-	0.043	$_{76}\text{Os}^{187}$

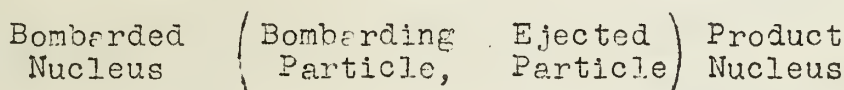
2. Artificial (induced) radioactivity---A perfectly stable nucleus can be converted into an unstable one by "bombardment" with suitable particles under suitable conditions. The missiles used for this purpose are tabulated below:

Name	Symbol	Nature
γ -, or X-ray	γ	High-energy γ - or X-radiation
neutron	n	${}_0n^1$
proton	p	${}_1H^1$ (or H^+)
deuteron	d	${}_1D^2$ (or D^+)
triton	t	${}_1T^3$ (or T^+)
α -particle	α	${}_2He^4$ (or $(He^4)^{++}$)

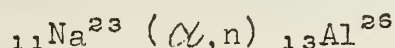
These particles, usually accelerated to high energies, are allowed to impinge upon a "target" of the nuclei to be bombarded. An example is the bombardment of Na with α -particles to give a radioactive isotope of Al:



A simpler system of notation has been adopted to represent these "nuclear reactions":



In the case being considered:



Incidentally, it is not to be concluded that all nuclear reactions result in radioactive nuclei. For example:

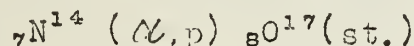


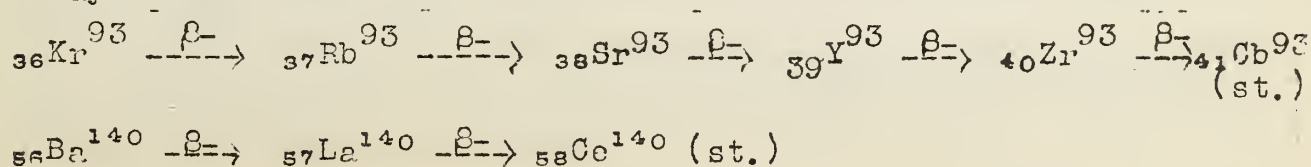
Fig. 3 shows the displacement in mass and nuclear charge sustained by a nucleus in undergoing a large number of these various transformations.

In general, nuclear reactions may be classified in 3 main categories:

a. Captures---in which the bombarding particle does not eject any massive particle, the term being necessarily restricted to $(n\gamma)$, $(p\gamma)$, $(d\gamma)$, $(t\gamma)$, $(\gamma\gamma)$, and radiationless captures.

b. Spallations---in which one or more relatively small particles is ejected leaving the bombarded nucleus essentially intact. The reactions given in Part IV. of this paper are of this type.

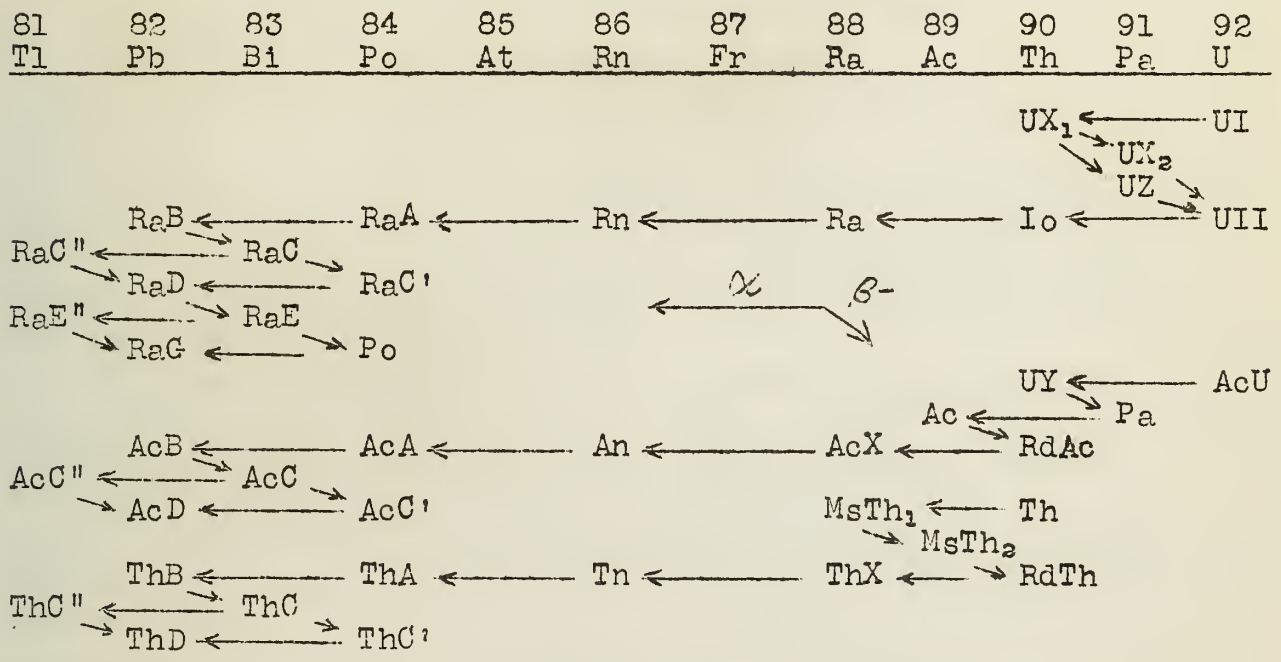
c. Fissions---in which the nucleus splits into 2 commensurate fragments, usually following a neutron capture; fission has been observed only in Pu^{239} , U^{235} , U^{238} , Pa^{231} , Th^{232} , and Bi^{209} . Clearly, since these nuclei all have high N:Z ratios, the 2 fragments (which will be in the lower ratio region) will necessarily have N:Z ratios that are too high. A typical example is given in Fig. 1 where U^{235} has undergone fission to produce ${}_{36}Kr^{93}$ and ${}_{58}Ba^{140}$ (2 neutrons having been lost in the process). In attaining stable N:Z ratios these nuclei must pass thru the following decay series:



Fission products of U are discussed in (8).

IV. Transformation Series Among the Heavy Nuclei

Actually, there is little to be discussed under this heading, the data being more efficiently presented in the accompanying tables and charts. The discovery of Po and Ra, the first radioactive elements known, by the Curies in 1898, was followed by the discovery of most of the rest of the naturally occurring unstable isotopes, and the working out of the 3 natural transformation series as follows:



Important constants for these series (and for the Np series, which does not occur in nature) are given below:

Series	Parent	Half Life of Parent	End Product	Decay		ΔA	ΔZ
				α	β		
Th(4n)	$^{232}_{90}\text{Th}$	1.39×10^{10} y.	$^{208}_{82}\text{Pb}$	6	4	-24	- 8
U(4n + 2)	$^{238}_{92}\text{U}$	4.51×10^9 y.	$^{206}_{82}\text{Pb}$	8	6	-32	-10
Ac(4n + 3)	$^{235}_{92}\text{U}$	7.07×10^8 y.	$^{207}_{83}\text{Bi}$	7	4	-28	-10
Np(4n + 1)	$^{237}_{93}\text{Np}$	2.25×10^6 y.	$^{209}_{83}\text{Bi}$	7	4	-28	-10

No additions were made to these tables for almost 20 years. It is the main purpose of this discussion to point out the extensions that have recently been made to these series:

1. The discovery by Perey of a branching α -decay of Ac to AcK, an isotope of element 87 (Fr) (6) (7). It is interesting to note that other workers observed this branch decay as early as 1914 (5), but World War I interrupted their investigations.
2. The discovery by Karlik and Bernert of branching β -decays of RaA, ThA, and AcA to isotopes of element 85, respectively At^{218} , At^{216} , and At^{215} (4).
3. The production of the missing (4n + 1) radioactive transformation series (1) (3). The parent (longest-lived) member of the series is Np^{239} , altho Pu^{241} is a higher member. These isotopes are produced as follows:

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71. $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$

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Journal of Management Education 26(7)

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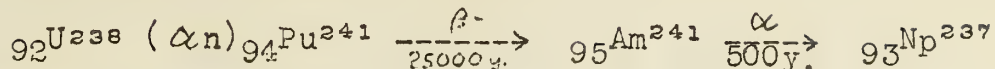
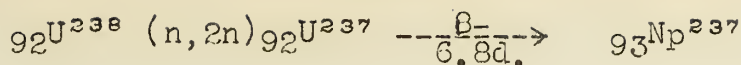
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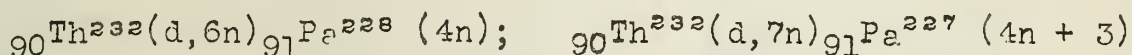
Important constants of this series are given in the table above, and some unique features follow:

a. The series passes directly thru isotopes of elements 87 (Fr) and 85 (At).

b. The series includes no isotope of Rn.

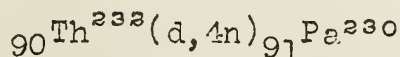
c. The series ends not with an isotope of Pb, but with Bi²⁰⁹.

4. By irradiation of Th with deuterons, 2 isotopes of Pa have been produced which initiate α -decay chains passing thru heretofore unknown isotopes of Ac and Fr, and joining the Th (4n) and Ac (4n + 3) series, respectively, at At²¹⁶ and At²¹⁵. These chains are said to be "collateral" to these families. The Pa isotopes are produced as follows:



It is believed to be certain that higher members of these collateral chains will eventually be produced (2).

5. A third isotope of Pa can also be obtained, this one passing thru U, Th, Pa, a new isotope of Rn (218), and RaC', there joining the U (4n + 2) series to which it is collateral (10). The reaction:



All these extensions are shown on the accompanying chart (broken lines) together with the long-established natural transformation series (solid lines). Important constants of all the nuclei are given in the table. (See also (9))

References:

- (1) English, A.C., Cranshaw, T.E., Demers, P., Harvey, J.A., Hincks, E.P., Jelley, J.V., and May, A.N.: Phys. Rev. 72 253-4 (1947)
- (2) Ghiorso, A., Meincke, W.W., and Seaborg, G.T.: *ibid.* 74 695-6 (1948)
- (3) Hagemann, F., Katzin, L.I., Studier, M.H., Ghiorso, A., and Seaborg, G.T.: *ibid.* 72 352 (1947)
- (4) Karlik, B. and Bernert, T.: Monatsh. 77 348-51 (1947); Naturwissenschaften 30 685-6 (1942); 31 298-9, 492 (1943); 32 44 (1944); 33 23 (1946); Z. Physik 123 51-72 (1944)
- (5) Meyer, S., Hess, V.F., and Paneth, F.A.: Sitzber. Akad. Wiss. Wien 123 IIa 1459-88 (1914)
- (6) Perey, M.: Compt. rend. 208 97-9 (1939); 214 797-9 (1942); J. chim. phys. 43 155-68, 262-8, 269-78 (1946)
- (7) Perey, M. and Lecoq, M.: Compt. rend. 212 893-5 (1941); J. phys. radium 10 439-40 (1939); Nature 144 326 (1939)
- (8) Plutonium Project: J. Am. Chem. Soc. 68 2411-42 (1946)
- (9) Seaborg, G.T. and Perlman, I.: Revs. Mod. Phys. 20 (Oct., 1948)
- (10) Studier, M.H. and Hyde, E.K.: Phys. Rev. 74 591-600 (1948)

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Constants of Heavy Nuclei Belonging to Transformation Series

| Name | Symb. | Half Life | Z | Element | A | Decay | Mev. |
|--|-------------------|-------------------------|----|---------|-----|-----------------------|-------|
| <u>THORIUM SERIES (4n)</u> | | | | | | | |
| Thorium | Th | 1.4×10^{10} y. | 90 | Th | 232 | α | 4.20 |
| (Abundance: 100%) | | | | | | | |
| Mesothorium 1 | MsTh ₁ | 6.7y. | 88 | Ra | 228 | β^- | 0.053 |
| Mesothorium 2 | MsTh ₂ | 6.13h. | 89 | Ac | 228 | $\beta^- (\gamma)$ | 1.55 |
| Radiothorium | RdTh | 1.90y. | 90 | Th | 228 | $\alpha (\gamma)$ | 5.42 |
| Thorium X | ThX | 3.64d. | 88 | Ra | 224 | α | 5.68 |
| Thoron | Tn | 54.5s. | 86 | Rn | 220 | α | 6.28 |
| Thorium A | ThA | 0.158s. | 84 | Po | 216 | α | 6.77 |
| (α : β^- = 1:1.34 $\times 10^{-4}$) | | | | | | β^- | |
| Astatine-216 | At ²¹⁶ | <1m. | 85 | At | 216 | α | 7.64 |
| Thorium B | ThB | 10.6h. | 82 | Pb | 212 | $\beta^- (\gamma)$ | 0.36 |
| Thorium C | ThC | 60.5m. | 83 | Bi | 212 | α | 6.05 |
| (34% α ; 66% β^-) | | | | | | $\beta^- (\gamma)$ | 2.20 |
| Thorium C' | ThC' | 0.3 μ s. | 84 | Po | 212 | α | 8.78 |
| Thorium C'' | ThC'' | 3.1m. | 81 | Tl | 208 | β^- | 1.72 |
| Thorium D | ThD | infinite | 82 | Pb | 208 | | |
| (Abundance: 52.29%) | | | | | | | |
| Protoactinium-228 | Pa ²²⁸ | 22h. | 91 | | | $\alpha (K)$ | 6.09 |
| Actinium-224 | Ac ²²⁴ | 2.5h. | 89 | | | $\alpha (K)$ | 6.17 |
| Francium-220 | Fr ²²⁰ | 30s. | 87 | | | α | 6.69 |
| <u>NEPTUNIUM SERIES (4n + 1)</u> | | | | | | | |
| Plutonium-241 | Pu ²⁴¹ | 25000y. | 94 | | | β^- | |
| Americium-241 | Am ²⁴¹ | 500y. | 95 | | | α | |
| Neptunium-237 | Np ²³⁷ | 2.25×10^6 y. | 93 | | | α | |
| Protoactinium-233 | Pa ²³³ | 27.4d. | 91 | | | $\beta^- (e, \gamma)$ | 0.2 |
| Uranium-233 | U ²³³ | 1.63×10^5 y. | 92 | | | α | 4.82 |
| Thorium-229 | Th ²²⁹ | 7000y. | 90 | | | α | 4.85 |
| Radium-225 | Ra ²²⁵ | 14.8d. | 88 | | | β^- | 0.2 |
| Actinium-225 | Ac ²²⁵ | 10.0d. | 89 | | | α | 5.80 |
| Francium-221 | Fr ²²¹ | 4.8m. | 87 | | | α | 6.50 |
| Astatine-217 | At ²¹⁷ | 0.020s. | 85 | | | α | 7.02 |
| Bismuth-213 | Bi ²¹³ | 47m. | 83 | | | α | 5.86 |
| (4% α ; 96% β^-) | | | | | | β^- | 1.2 |
| Polonium-213 | Po ²¹³ | 3.2 μ s. | 84 | | | α | 8.34 |
| Thallium-209 | Tl ²⁰⁹ | less than 1h. | 81 | | | β^- | |
| Lead-209 | Pb ²⁰⁹ | 3.3h. | 82 | | | β^- | 0.68 |
| Bismuth-209 | Bi ²⁰⁹ | infinite | 83 | | | | |
| (Abundance: 100%) | | | | | | | |
| <u>URANIUM SERIES (4n + 2)</u> | | | | | | | |
| Uranium I | UI | 4.51×10^9 y. | 92 | U | 238 | α | 4.2 |
| (Abundance: 99.274%) | | | | | | | |
| Uranium X ₁ | UX ₁ | 24.5d. | 90 | Th | 234 | $\beta^- (\gamma)$ | 0.190 |
| | | | | | | (0.09) | |
| Uranium X ₂ | UX ₂ | 1.14m. | 91 | Pa | 234 | $\beta^- (\gamma)$ | 2.32 |
| | | | | | | (0.8) | |
| | | | | | | I.T. | |
| Uranium Z | UZ | 6.7h. | 91 | Pa | 234 | $\beta^- (\gamma)$ | 0.5, |
| | | | | | | 1.2 (0.8) | |
| Uranium II | UII | 2.33×10^5 y. | 92 | U | 234 | α | 4.75 |
| (Abundance: 0.00518%) | | | | | | | |
| Ionium | Io | 8.3×10^4 y. | 90 | Th | 230 | $\alpha (\gamma)$ | 4.66 |
| Radium | Ra | 1590y. | 88 | Ra | 226 | $\alpha (\gamma)$ | 4.29 |
| | | | | | | (0.19) | |

| Name | Symb. | Half Life | Z | Element | A | Decay | Mev. |
|---|-------------------|--------------------------|----|---------|-----|---|-----------------------|
| Radon | Rn | 3.825d. | 86 | Rn | 222 | α | 5.49 |
| Radium A
($\alpha:\beta^- = 1.4 \times 10^{-4}$) | RaA | 3.05m. | 84 | Po | 218 | α
β^- | 6.00 |
| Astatine-218 | At ²¹⁸ | few s. | 85 | | | α | 6.63 |
| Radium B | RaB | 26.8m. | 82 | Pb | 214 | $\beta-(\gamma)$ | 0.65 |
| Radium C
(0.03% α ; 99.97% β^-) | RaC | 19.7m. | 83 | Bi | 214 | α
$\beta-(\gamma)$ | 5.50
3.15
(1.0) |
| Radium C' | RaC' | 150us. | 84 | Po | 214 | α | 7.68 |
| Radium C'' | RaC'' | 1.32m. | 81 | Tl | 210 | β^- | 1.80 |
| Radium D | RaD | 22y. | 82 | Pb | 210 | $\beta-(\gamma)$ | 0.065
(0.047) |
| Radium E | RaE | 5.0d. | 83 | Bi | 210 | $\alpha(\beta^-)$ | 4.87
(1.1) |
| Radium F | RaF | 140d. | 84 | Po | 210 | $\alpha(\gamma)$ | 5.30
(0.8) |
| Radium E'' | RaE'' | 4.23m. | 81 | Tl | 206 | $\beta-(\text{no } \gamma)$ | 1.7 |
| Radium G
(Abundance: 23.59%) | RaG | infinite | 82 | Pb | 206 | | |
| Protoactinium-230 | Pa ²³⁰ | 17d. | 91 | | | β^- | |
| Uranium-230 | U ²³⁰ | 20.8d. | 92 | | | α | 5.86 |
| Thorium-226 | Th ²²⁶ | 30.9m. | 90 | | | α | 6.3 |
| Radium-222 | Ra ²²² | 38s. | 88 | | | α | 6.5 |
| Radon-218 | Rn ²¹⁸ | 0.019s. | 86 | | | α | 7.1 |
| <u>ACTINIUM SERIES (4n + 3)</u> | | | | | | | |
| Actino-Uranium
(Abundance: 0.719%) | AcU | 7.07×10^8 y. | 92 | U | 235 | α | 4.52 |
| Uranium-Y | UY | 24.6h. | 90 | Th | 231 | β^- | 0.2 |
| Protoactinium | Pa | 3.2×10^4 y. | 91 | Pa | 231 | α | 5.00
4.72
4.69 |
| Actinium
(1.2% α ; 98.8% β^-) | Ac | 13.5y. | 89 | Ac | 227 | α
$\beta-(\text{no } \gamma)$ | 5.0 |
| Radioactinium | RdAc | 18.9d. | 90 | Th | 227 | $\alpha(\gamma)$ | 6.05 |
| Actinium K | AcK | 21m. | 87 | Fr | 223 | $\beta-(\gamma)$ | 1.32
(0.16) |
| Actinium X | AcX | 11.2d. | 88 | Ra | 223 | $\alpha(\gamma)$ | 6.12 |
| Actinon | An | 3.92s. | 86 | Rn | 219 | α | 6.82 |
| Actinium A' | AcA | 1.83×10^{-3} s. | 84 | Po | 215 | α
β^- | 7.86 |
| ($\alpha:\beta^- = 1:5 \times 10^{-6}$) | | | | | | | |
| Astatine-215 | At ²¹⁵ | cc. 10^{-4} s. | 85 | | | α | 8.00 |
| Actinium B | AcB | 36.1m. | 82 | Pb | 211 | $\beta-(\gamma)$ | 0.5
1.4
(0.8) |
| Actinium C | AcC | 2.16m. | 83 | Bi | 211 | α
$\beta-(\gamma)$ | 0.69 |
| (99.7% α ; 0.3% β^-) | | | | | | | |
| Actinium C' | AcC' | 5×10^{-3} s. | 84 | Po | 211 | α | 7.45 |
| Actinium C'' | AcC'' | 4.76m. | 81 | Tl | 207 | $\beta-(\gamma)$ | 1.47 |
| Actinium D
(Abundance: 22.64%) | AcD | infinite | 82 | Pb | 207 | | |
| Protoactinium-227 | Pa ²²⁷ | 38m. | 91 | | | $\alpha(K)$ | 6.46 |
| Actinium-223 | Ac ²²³ | cc. 2m. | 89 | | | α | 6.6 |
| Francium-219 | Fr ²¹⁹ | cc. 10^{-4} s. | 87 | | | α | 7.80 |

15 March 1949

Charles J. Hoffman

I. Introduction: The magnetic behavior of matter in the bulk-- para-magnetism, diamagnetism, and ferromagnetism--can be traced to the electronic structure of the atoms of which the matter is composed. The electron, in short, is the cause of ordinary magnetism. But the electron is not the only magnetic constituent of most substance for many atomic nuclei have certain magnetic properties. Although the magnetic effects to which these nuclear properties give rise are too feeble to be observed under most circumstances, it has been possible to devise techniques which bring them into prominence. From these experiments in nuclear magnetism one can learn:

1. More about the nucleus, and
2. The Structure of solids and liquids.

II. Nuclear Spins and Magnetic Moments¹⁰ In addition to their more familiar properties of mass and electric charge, many atomic nuclei possess intrinsic angular momentum, or "spin," and magnetic moment; that is to say, the nucleus behaves like a spinning top with a magnet embedded along its axis. The origin of the nuclear magnetism is in the motion of the positive electric charge of the nucleus; charge in motion is the same as electric current, and electric currents produce magnetic fields. We can regard the proton, for example, as a positively charged sphere spinning with a certain angular momentum and equivalent, in its magnetic properties to an infinitesimal magnetic dipole.

The energy differences involved in the interaction of the nuclear magnet with the surrounding electrons are usually not larger than 10^{-20} ergs. According to the Bohr relation,

$$\Delta E = h\nu \quad (h = \text{Planck's constant})$$

the corresponding frequencies lie in the band of ordinary radio frequencies. The possibility is thereby suggested of measuring such weak interactions directly, by detecting the absorption or emission of waves of radio frequency. Rabi and co-workers¹ have used this means to determine the spins of several nuclear species.

| Nucleus | I (spin) | Nucleus | I (spin) |
|----------------|----------|------------------|----------|
| 1O^1 | $1/2$ | 4Be^9 | $3/2$ |
| 1H^1 | $1/2$ | 5B^{10} | 1 |
| 1H^2 | 1 | 5B^{11} | $3/2$ |
| 2He^3 | $1/2$ | 6C^{12} | 0 |
| 2He^4 | 0 | 6C^{13} | $1/2$ |
| 3Li^6 | 1 | 7N^{14} | 1 |
| 3Li^7 | $3/2$ | 7N^{15} | $1/2$ |
| | | 8O^{16} | 0 |

III. Resonance Absorption The emission or absorption of light by a free atom takes place in accordance with the resonance condition which quantum theory permits us to express in the following way: The possible states of an isolated atom include a sequence of discrete states sharply defined with respect to energy; a transition

of the system from one of these states to another, differing in energy from the first by ΔE , is accompanied by emission (or absorption) of light of the frequency

$$\nu = \frac{\Delta E}{h} \quad (h = \text{Planck's constant})$$

Let us consider a free proton in a magnetic field of strength H_0 . Ignoring the translational degrees of freedom, which are here irrelevant, this simple system will be found in one of two possible states which differ in the orientation of the spin axis of the proton with respect to the magnetic field. That is, the component, in the direction of the magnetic field, of the angular momentum vector can assume either of the values $+\hbar/4\pi$ or $-\hbar/4\pi$. The two states differ in energy, for the component of nuclear magnetic moment in the direction of the field is $+\mu$ in one case and $-\mu$ in the other. In fact, the difference in energy, ΔE is just $2\mu H_0$, the work that would be necessary to reverse the direction of a magnet of strength μ which had originally been aligned with a field H_0 . The states will be denoted by (+) and (-), the (-) referring to the state of higher energy in which the nuclear magnet is directed counter to the magnetic field.

By exposing the system to radiation of the proper frequency, it should be possible to bring about a transition from one of the two states to the other, with the consequent absorption of a quantum of energy, in a (+) to (-) transition, or emission of a quantum, in a (-) to (+) transition. For a proton in a magnetic field H_0 , of 10,000 gauss, the resonance frequency computed from

$$\nu = \frac{\Delta E}{h} = \frac{2\mu H_0}{h}$$

is about 41 megacycles/sec.

IV. Experimental Apparatus 2, 3, 4, 5 The method of observation is extremely simple in principle. To illustrate let us take water which contains hydrogen nuclei and oxygen nuclei. However only the hydrogen nuclei have spin so we can neglect the oxygen nuclei. Approximately 0.5 cc of water contained in a glass tube, is surrounded by a coil consisting of a few turns of copper wire. The coil is connected into a radio-frequency bridge circuit which is excited by an oscillator at, say 40 Mc/sec. The coil with its water "core" is located within the field of a strong magnet. When resonance conditions are attained by adjustment of the frequency, the absorption of energy by the protons in the water is manifested as a change in the apparent resistance of the coil. Because the effect to be detected is extremely feeble the apparatus is actually more elaborate than the description might suggest.

V. Interpretation of Line Width and Line Structure The nuclei are, of course, not entirely isolated from magnetic disturbances of local origin. The most obvious sources of perturbing magnetic fields are the magnetic nuclei themselves. A selected proton in a drop of water is subject not only to any field which we may apply with an electromagnet, but also the magnetic fields arising from the magnetic moments of neighboring protons in the liquid, including that of the other proton in the same water molecule. The sum of all such perturbing fields, measured at the location of a given proton--but, of course, excluding the field of that proton--we shall call the "local field" H_{loc} . The local field will vary in magnitude and direction, from point to point in the material

THEORY OF THE EARTH

The theory of the earth is a branch of geology which deals with the origin and development of the earth and its various parts. It is a science which seeks to explain the processes which have shaped the earth and its features. The theory of the earth is based on the study of the earth's history and its various parts. It is a science which seeks to explain the processes which have shaped the earth and its features. The theory of the earth is based on the study of the earth's history and its various parts. It is a science which seeks to explain the processes which have shaped the earth and its features.

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A dipole can represent the z-component of the magnetic moment of a proton in the state (-). Let us consider only the z-component of the field produced by the dipole, , at some nearby point P which might be the location of another proton. This component of the local field at P is given by

$$(H_{loc})_z = \frac{\pm \mu}{r^3} (3 \cos^2 \theta - 1)$$

where θ is the angle between the z-axis and point P. Thus the total magnetic field, in the z-direction, that would be experienced by another proton located at P, is

$$H_0 \pm \frac{\mu}{r^3} (3 \cos^2 \theta - 1)$$

The effect of the neighboring protons is thus to alter slightly, the total magnetic field experienced by a selected proton. Only the nearest neighbors will contribute significantly to H_{loc} because of the inverse-cube dependence and angular dependence of the dipole field.

Four resonance components were observed by Pake⁶ in a single crystal of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) when the crystal was orientated in a particular way with respect to the direction of the strong magnetic field. The only important magnetic nuclei in gypsum are the protons in the molecules of water of hydration. The crystal structure of gypsum has been well established through the analysis of Wooster⁷, but it will be recalled the X-ray diffraction yields no direct evidence of the location of protons in a crystal. Nevertheless, there is reason to assume that each proton has one near magnetic neighbor, the other proton belonging to the HOH molecule, and that the next nearest proton neighbor is considerably further away. The angle θ is now the angle between the H-H line in an HOH molecule and the magnetic field H_0 . As it turns out, there are only two distinct H-H directions in a gypsum crystal; that is, for a given orientation of the single crystal in the magnet, θ has the same value for half the molecules in the crystal. From the protons in these molecules we should therefore expect a pair of resonance lines, symmetrically displaced to either side of the central position that would be determined by single proton with no perturbing fields. The remainder of the molecules, to which a different value of θ applies, should give rise to another pair of lines, thus four lines in all. Each of these lines will be smeared out somewhat by the hitherto neglected fields of the more distant neighbors. This is just what was observed. Moreover, as the crystal was rotated in the apparatus, the separation of the components was found to vary precisely in accordance with the factor $3 \cos^2 \theta - 1$. From these observations, interpreted with the aid of a theory⁶, 11 more rigorous than given here, it is possible to determine not only the directions of the H-H lines with respect to the crystal axes, but also, with a precision of about 1%, the distance between the two protons in the HOH molecule--information which the X-ray analysis does not yield.

Using methods similar to those outlined above, certain aspects of molecular and crystal structure have also been studied^{8,9,10}.

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William R. Miller

22 March 1949

Introduction

The first investigations of the hydrides of boron were carried out toward the end of the last century, and were attended by many difficulties due to the volatile and unstable characteristics of these compounds. Beginning in 1912 and continuing for the next twenty-five years, Stock and co-workers did the classical investigations in this field. This work is summarized in Stock's treatise on the subject, which may be considered to be the definitive reference on the boranes (1). Most of the information to be presented, not otherwise credited, is derived from this source.

Present day interest in the boranes is centered on the structural problems presented by these compounds and on certain new reactions of the boranes. New syntheses have been developed for diborane. This seminar will outline the advances in this field in the last two years.

Properties of the Boron Hydrides

Table I lists the physical constants of the boranes:

Table I (2)
Physical Constants of the Boranes

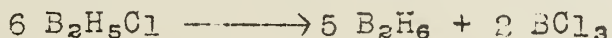
| Name | Formula | MP | BP |
|----------------------|---------------------------------|---------|-------------------|
| Diborane | B ₂ H ₆ | -165.5° | -92.5° |
| Tetraborane | B ₄ H ₁₀ | -120 | 18 |
| Stable pentaborane | B ₅ H ₉ | - 46.6 | 48 |
| Unstable pentaborane | B ₅ H ₁₁ | -123 | 63 |
| Hexaborane | B ₆ H ₁₀ | - 65 | (VP at 0°, 7.2mm) |
| Decaborane | B ₁₀ H ₁₄ | 99.7 | 213 |

Certain other boranes are known but they have been obtained in such small quantities that their properties have not been determined. The boranes listed in Table I are colorless and have disagreeable odors (1).

Preparation

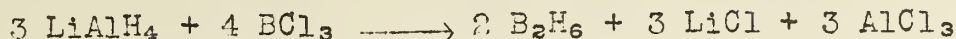
Treatment of magnesium boride with hydrochloric or phosphoric acid gives a mixture of boranes. Tetraborane is the chief component of this mixture. Small quantities of the stable pentaborane, hexaborane and decaborane are also obtained.

Diborane, which is instantly decomposed in the presence of moisture, is not obtained in this manner. It may be prepared by the thermal decomposition of tetraborane. A newer method consists of passing a current of hydrogen and boron chloride through an electrical discharge (3). The product of this reaction is some diborane and a great deal of B₂H₅Cl. The latter compound rapidly undergoes disproportionation into diborane and boron chloride:



A still newer method involves the reduction of boron halides by hydrogen in the presence of an active metal at 300°. The metals used included aluminum, magnesium, zinc and sodium (4). A similar reduction may be carried out using sodium or calcium hydride. In this case the hydride is the active reducing agent.

Diborane can be produced most readily and quantitatively by the interaction of boron chloride with lithium aluminum hydride(5):

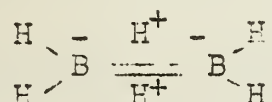


The other boranes are prepared by heating either tetraborane or diborane at various temperatures for various lengths of time. The conditions for these conversions are entirely empirical and there is no definite information with regard to mechanism. Free radicals are presumed to be involved (2).

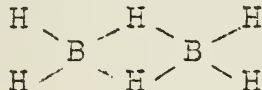
Structure

Most of the evidence for the structure of the boranes is physical in nature, being based on spectrographic, electron diffraction and X-ray data. The boranes cannot have the apparent structures due to the fact that they are electron-deficient compounds, i.e., they have fewer than the number of electrons required to account for the bonds in the apparent structures.

Pitzer, in 1945, suggested the protonated double bond configuration for diborane (6):



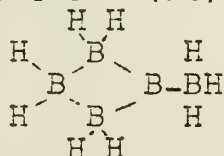
An obvious objection to this structure is that diborane has no acidic properties (7). An alternative structure may be found in the bridge model (reference 2 gives a short discussion of the background of this model):



This configuration is supported by electron diffraction (8), infrared (9) and Raman spectra (10).

At present, it seems that the above two structures are being considered as identical, the main point of contention involving use of the term "protonated" (11). Pauling, in considering tetramethyldiborane, states that, if the bonds between the methyls and boron are single covalent bonds, enough electrons are left for two additional electron-pair bonds for which there are five positions available: one between the two borons and four between boron and hydrogen. Calculations, assuming equal resonance, give a B-B distance of 1.85 Angstrom units, exactly the distance found experimentally (12).

Electron diffraction evidence seems to favor the following configuration for pentaborane (13):



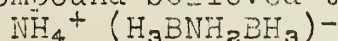
The structure of decaborane has been the subject of an extensive study by Silbiger and Bauer (13). They compared the electron diffraction patterns of decaborane with those calculated for ten possible structures and came to the conclusion that the decaborane molecule is made up of two pentagons joined in parallel planes. However, Kasper, Lucht and Harker, in studying X-ray diffraction patterns, have found the decaborane molecule to be much more complicated (14). These authors have suggested a three-dimensional model in which each hydrogen, except two, is joined to a single boron and each boron is bound to five or six other atoms but the

bonds are not equivalent. This model is in agreement with the calculations of Silbiger and Bauer but was not considered by them due to its unexpected form(13).

Little has been done with regard to the structure of the other boranes. Pitzer has suggested structures for these compounds, based on his theory of the protonated double bond (6). No experimental evidence has been put forward either favoring or contradicting these structures.

Reactions

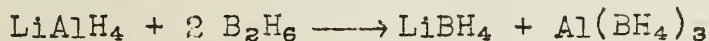
The boranes undergo a number of typical reactions, most of which were studied extensively by Stock (1). All of the boranes are decomposed at red heat into boron and hydrogen. All undergo hydrolysis but the ease of hydrolysis varies. Diborane, for example, is decomposed instantly while decaborane will react with water only on prolonged heating. The boranes are halogenated either with free halogen or hydrogen halide. Diborane reacts with ammonia to form a compound believed to be



Diborane reacts with amalgams, as do tetraborane and pentaborane, to form sodium derivatives



It has recently been found that diborane will react with lithium aluminum hydride to form lithium and aluminum borohydrides (5):



The reactions of diborane with hydrocarbons have been studied recently (15). The reactions tend to be complex and must be run using a large excess of hydrocarbon to minimize the effect of the highly reactive diborane which is usually present to the extent of about two to ten percent by weight in the reaction mixture. Several different reactions have been observed:

1. The addition of diborane to olefins occurs with saturation of the double bonds and the formation of trialkyls of boron.

2. Substitution on the benzene ring occurs with the formation of phenylboron compounds.

3. Diborane reacts with paraffins to form polymeric reaction products containing boron, carbon and hydrogen. Breakdown and synthesis of hydrocarbon chains is effected in these reactions.

Isobutylene, for example, gives tri-t-butyl- and triisobutylboron. Ethylene gives triethylboron. Benzene gives triphenylboron. When methane is heated with diborane, ethane, propane and butane are found in the products of reaction as well as volatile methylboron compounds.

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-air-

Since electrochemical reactions are of such great importance commercially and since they constitute an important type of chemical reaction, a knowledge of the mechanisms involved should be of great value, both practically and theoretically.

In the deposition of a metal ion, the potential of the electrode should be determined by the equilibrium between the oxidized and reduced species (1). This potential can be calculated from the standard potential by the use of the Nernst equation. When the potential of the electrode is made more negative than the equilibrium or reversible potential a current tends to flow in an attempt to bring the potential back to the equilibrium value. If the potential is not brought back to the equilibrium potential, one of the steps in the process must be too slow to allow equilibrium to be reached, and the electrode is said to be polarized.

There are three general processes involved in the polarization of an electrode in the reduction of a metal ion: (a) supply of ions to the surface of the electrode by diffusion, convection, or movement of the solution, (b) discharge of ions on the surface of the electrode, and (c) disposal of reduced ions (2). In deposition of a metal ion from a solution at high current density or at a small electrode, the supply of ions at the surface of the electrode is usually reduced more rapidly than the ions can diffuse to the electrode. Films, adsorbed layers, or precipitated layers on the electrode may also prevent a sufficient supply of ions from reaching the surface. In some cases, the actual acceptance of one or more electrons by the ion is slow, possibly due to the necessity for the ions to become oriented in some special way to the electrode.

The third factor, disposal of the reduced ions, can be especially important in the deposition of metals because the atoms must deposit on the electrode in a definite crystalline arrangement. This may act as the slow stage of the deposition and thereby affect the potential of the electrode.

Salt (3) has studied the overvoltage of nickel deposition at various hydrogen ion concentrations, at various temperatures, and at various current densities. The overvoltages varied from about 0.2 to 0.8 volts in a complex way as the conditions were varied. From this data it was impossible to determine the actual mechanism of the overvoltage.

Finch, Wilman and Yang, (4) have made a careful study of crystal growth at the cathode. When a metal atom is discharged at a cathode it must assume a position in relation to the other atoms already deposited which is in accord with the crystal structure of the metal. The mechanism of this orientation is of importance in relation to its effect on the polarization of the electrode, as well as of great practical importance in relation to the properties and adherence of electrodeposited metal layers. A comparison of three conditions for crystal growth show the factors affecting electrodeposition. (a) deposition in low pressure gas--atoms being deposited on the surface have mobility characteristic of the substrate material and of the temperature; (b) crystallization from solution--mobility greater than in (a) due to impacts of the solvent molecules; (c) electrodeposition--mobility about the same as (b) except for increased rate of deposition on electrode surface projections due to the concentration of the charge there.

These differences produce characteristically different types of deposits.

In general, the factors affecting the crystal growth are dependent partly on the bath conditions and partly on the substrate. Those factors depending primarily on the former are (a) rate of arrival of the metal ions, (b) their mobility on the cathode surface before becoming a part of a growing crystal, (c) the presence or absence of other ions, molecules, or colloidal substances which can be adsorbed or codeposited on the surface. These factors are related to the bath concentration, temperature, and motion (due to stirring or convection), and on the current density and distribution on the cathode. The substrate effects are caused by the atomic arrangement of the substrate surface and by the concentration of the charge at the projections of the cathode surface.

Stages of Cathodic Crystal Growth

A. Initial Stage

Three different types of substrate surface--single crystal, polycrystalline, and amorphous--were used in studying the orientation of the deposited metal. In depositing copper on a smooth single copper crystal, electron diffraction patterns indicated that at an average deposit thickness of 200 Angstroms, the deposit maintained the structure of the original crystal both in crystal orientation and lattice perfection, the only difference being that the surface had become rather rough. The same conditions prevailed at 500Å. except that the surface had become even rougher. Similar investigations of the deposition of other metals on Cu or Fe single crystals indicate similar lattice continuation in cases where the lattice spacings of the two metals along the contact face in parallel directions differ by less than 15%. On random or oriented polycrystalline substrate surfaces parallel growth occurred when the deposit and substrate had nearly the same lattice dimensions. On amorphous surfaces, prepared by mechanically polishing the cathode surface, thin deposits had random polycrystalline structure.

B. Transition Stage

After the electrodeposited layer, whose structure is first determined by the substrate, has grown for some time, the orienting influence of the substrate becomes weakened enough so that gradually the structure becomes more random. The thickness of the layer when this effect first becomes noticeable varies greatly with the conditions. Slow deposition on a single crystal may allow layers as thick as 40,000 Å. to form before any change is apparent, while on a polycrystalline substrate composed of small crystals the initial stage may extend to a thickness of only 1000-2000 Å.

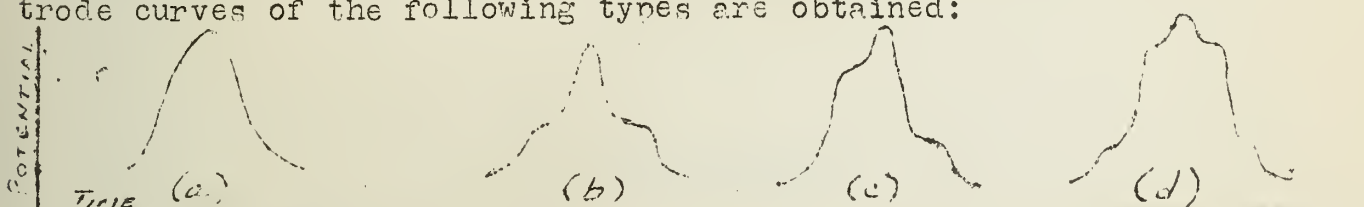
C. Final Stage

The transition stage layer does not extend more than a few thousand Å., after which the deposit assumes an orientation determined by the bath conditions. Once the final stage is established the orientation is independent of the thickness of the layer. Depending on the metal deposited and the bath conditions used, amorphous, random polycrystalline, or crystalline deposits with a definite orientation to the substrate surface can be obtained. Metals with low cohesive forces, such as Sb and As, tend to form amorphous deposits. Most metals give random crystalline deposits under conditions which cause the deposition to be accompanied by the evolution of considerable hydrogen.

In deposits which assume an orientation in relation to the substrate surface, high mobility of the deposited atoms over the surface favors the formation of crystals with the most densely-packed lattice-planes parallel to the substrate surface, while low mobility tends to favor the formation of crystals with these densely-packed planes perpendicular to the substrate surface. This latter case tends to favor the growth on the surface projections, thereby giving a rough deposit. The action of colloidal materials and organic addition agents is presumed to be due to the adsorption of these materials on the projections

Alternating Current Polarography

A relatively new method for the study of electrode reactions is the use of alternating current for polarographic measurements (5). If an alternating current is passed through a dropping mercury electrode curves of the following types are obtained:



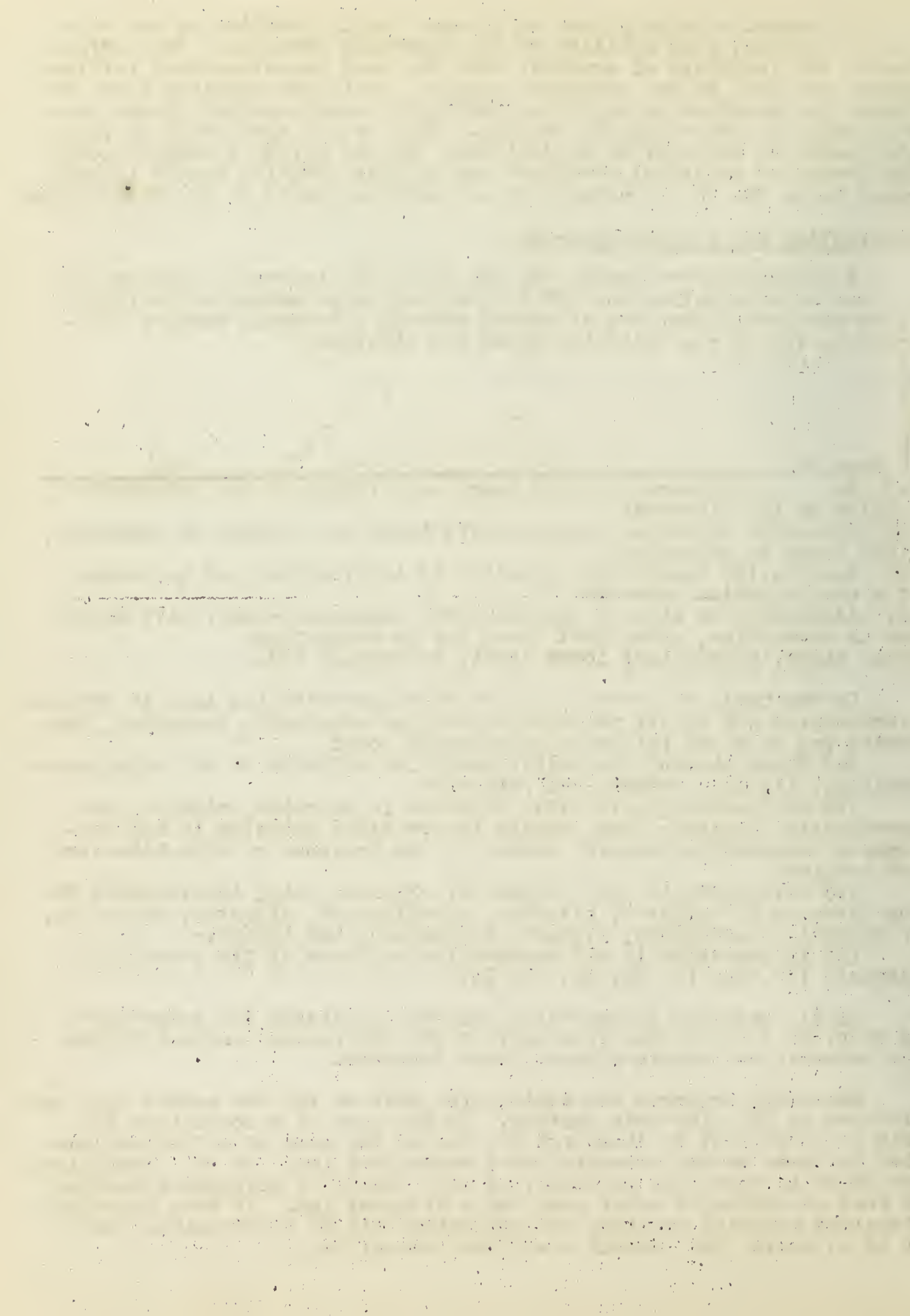
- (a) No substances present which will reduce at the potentials applied to the electrode
- (b) Reducible substance present--left break corresponds to reduction, right break to oxidation.
- (c) Same as (b) except the reduction is irreversible and so occurs at a more negative potential
- (d) Adsorption of film of non-reducible substance--lower left break due to adsorption, upper left break due to desorption. Upper right, adsorption; lower right, desorption (6).

On the basis of curves of these types for metallic ions in various electrolytes and in the presence of various adsorbable compounds, Heyrovsky has made the following grouping of ions:

- (a) Those showing reversible reduction behavior in all solutions--thallous, lithium, sodium, and potassium
- (b) Ions showing reversible behavior in chloride, nitrate, and perchlorate solutions, but showing irreversible behavior in the presence of adsorbable material except in the presence of chloride--lead and cadmium
- (c) Reversible in the presence of chloride only; irreversible in the presence of sulfates, nitrates, perchlorates, citrates, tartrates, or hydroxides--stannous, bismuth, antimonous, and indium.
- (d) Irreversible in all cases--divalent ions of the transition elements (Cr, Mn, Fe, Co, Ni, Cu, Zn)

In all cases of irreversible reduction, raising the temperature to 90°C. or lowering the frequency of the alternating current brings the cathodic and anodic breaks closer together.

Heyrovsky proposes the explanation that an ion can accept only one electron at the electrode surface. In the case of a monovalent ion this is sufficient to discharge it, but in the case of a divalent cation it leads to the formation of a monovalent ion. If this monovalent ion which is formed is unstable, it will undergo a disproportionation to form an uncharged metal atom and a divalent ion. If this disproportionation reaction is slow, the reduction will be irreversible, while if it is rapid, the reduction will be reversible.



The effect of the adsorbed films is proposed to be due to the hindrance of the disproportionation reaction, thereby causing ordinarily reversible reactions to become irreversible. Chloride ions supposedly serve to transfer electrons from the cathode to the ion or from one ion to another and thereby counteract the effect of the adsorbed film. Frumkin (7), however, has criticized this view, and proposes that the effect of the chloride is simply due to the changes in the double layer structure when anions are adsorbed.

By a modification of the electrical circuit it is possible to obtain curves which represent the derivatives of the potential-time curves. The rate of deposition of the metal ion can be measured graphically from these curves, thus allowing a quantitative determination of this rate. By this means the effect of the adsorbed films in slowing down the reduction rate is clearly shown.

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REACTIONS IN ANHYDROUS HYDROGEN CYANIDE

H. A. DeWalt, Jr.

April 5, 1949

I. Introduction: Liquid hydrogen cyanide has been studied as a non-aqueous, water like solvent primarily because at its 26° boiling point and its relatively high dielectric constant. An appreciable number of inorganic and organic compounds have been found to be soluble in it as predicted by the Nernst-Thomson Rule (1,2). Prior to the work of Jander and Scholz (3) only a few investigations had been carried out involving molecular weight determinations, conductometric and potentiometric titrations, and reactions in liquid HCN.

II. Preparations and Properties of HCN. Liquid HCN is prepared by passing the dried gas through a spiral condenser which is cooled to 0°. Gaseous hydrogen cyanide can be prepared by the action of sulfuric acid on potassium hexacyanoferrate (II), potassium cyanide (4,5), or sodium cyanide (6,8). The heat of the reaction is sufficient to force the gaseous hydrogen cyanide from the reaction flask through several calcium chloride filled drying tubes and into the condenser. The last traces of moisture are removed by treatment with phosphorous (V) oxide. Decantation and distillation give anhydrous HCN which is stabilized by addition of dry calcium chloride.

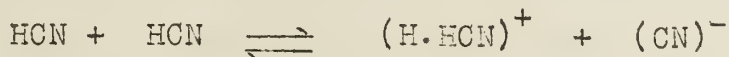
The physical constants of water and anhydrous hydrogen cyanide are listed in the following table:

| | Electrical Con-
ductivity in
Ohm ⁻¹ | M.P. | B.P. | Heat of
fusion
Kcal/mole | Molal Freez-
ing point
depression | Dielec-
tric
Constant |
|------------------|--|--------|-------|--------------------------------|---|-----------------------------|
| H ₂ O | 6 x 10 ⁻⁸ (25°) | 0° | 100° | 1.43 | 1.86 | 81 ^{18°} |
| HCN | 45 x 10 ⁻⁸ (0°) | -13.4° | 25.6° | 2.009 | 1.805 | 123 ^{15.6°} |

Coates (10) made a study of the variation of the dielectric constant of liquid hydrogen cyanide with temperature and found that the dielectric constant and its temperature coefficient were abnormally high. This abnormality is due to hydrogen bonding which produces transitory linear polymers of high dipole moment. A decreasing dielectric constant with increasing temperature showed that the mean length of these polymers is shortened by thermal agitation.

Raman spectra studies by Herzbergh (12) show that if hydrogen isocyanide, HNC, is present in liquid HCN its concentrations must be considerably less than that of the isotopic C¹³ hydrogen cyanide.

III. Neutralization Reactions. In analogy to the aquo system the slight conductance of pure liquid HCN must be due to the following auto-ionization process:

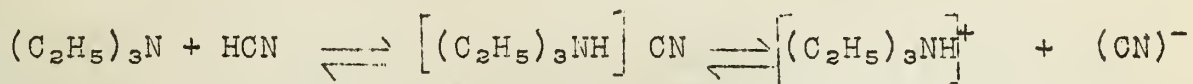


Any substance capable of dissociating protons in liquid HCN is called an acid analogue, while those substances which yield cyanide ions are called base analogues.

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Perchloric, sulfuric, nitric, dichloroacetic, and picric acids are all soluble in liquid HCN and behave as acids.

Alkali cyanides and organic amines, such as triethylamine and propylamine are soluble and act as base analogues. To function as base analogues, these organic amines must first react with the solvent to produce the substituted ammonium cyanides which then dissociate as follows:



Strong organic amines react to a large extent with the formation of the "onium" and cyanide ions.

To prove that the acids analogues and base analogues of the cyano system react in liquid HCN to form a salt and the slightly dissociated parent solvent, Jander and Coworkers (3,13) followed the course of neutralization reactions by means of conductometric titrations. Graphical representation of these results showed that the breaks in the conductivity curves correspond to the stoichiometric amounts of acid and base. Graphs similar to those observed in the aquo-system for the titration of various strength acids and bases were also obtained. By this method, Jander (3,13) obtained curves for neutralization of perchloric, sulfuric, nitric, dichloroacetic acids by potassium cyanide and triethylamine.

The salts produced by these neutralization reactions were actually isolated and identified.

IV. Behavior of Indicators in liquid HCN. The use of indicators was first investigated by Jander (13). Many known indicators are soluble in HCN. The color of the solutions depends on the hydrogen ion concentration as illustrated by the data given in the following table:

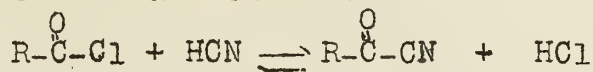
| Indicator | Color in liquid HCN | | pH transition in H ₂ O | Color in Water | |
|-----------------|---------------------|-------------|-----------------------------------|----------------|--------|
| | Acid | Base | | Acid | Base |
| Thymol-blue | Red | Red | greenish-yellow 1.2-2.8 | Red | Yellow |
| Methyl Red | Red | Red | yellow 4.2-6.3 | Red | Yellow |
| Phenol-Red | Red-orange | light-red | red 6.8-8.4 | yellow | red |
| Alizarin-yellow | yellow | pale-yellow | yellow 10.1-12.1 | yellow | red |

Conductivity studies demonstrated that acids soluble in HCN could be arranged in the following order of acid strengths: $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{CHCl}_2\text{CO}_2\text{H} > \text{picric acid}$. Perchloric acid is the strongest electrolyte while sulfuric and nitric are only moderately strong electrolytes. Dichloroacetic and picric acids are weak electrolytes and are incapable of producing an indicator change. Nitric acid was found to attack indicators. Solutions of perchloric acid in HCN are unstable. For these reasons only sulfuric acid could be studied for the purpose of ascertaining indicator color changes.

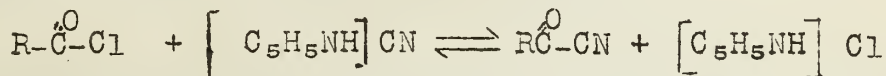
Conductance measurements also showed that the alkali cyanides and the strong organic amines are good electrolytes in HCN. Triethylamine was used as the basic analogues in the indicator color change studies since the alkali cyanides have a tendency to decolorize the solvent.

V. Solvolytic Reactions: In analogy to the aquo-system, solvolytic reactions can be divided into two main classes:

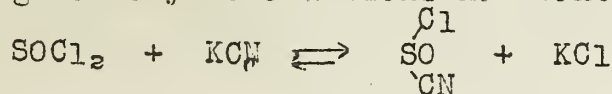
A. Solvolysis of Acid Chlorides: Organic acid chlorides react with the solvent as follows:



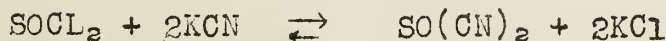
The position of the equilibrium is well on the side of the free acid chloride. However, Jander and Coworkers (3) forced the equilibrium to right in the case of acetyl and benzoyl chlorides by adding sufficient pyridine to react completely with the liberated hydrogen chloride. Both acetyl and benzoyl cyanides were isolated in excellent yields. In the presence of pyridine the reaction must proceed as follows:



Solvolysis of thionyl chloride in the presence of 2 moles of potassium cyanide should theoretically yield a mixture of thionyl chloro-cyanide and thionyl cyanide. Potentiometric titrations and isolation of 1.75 moles of potassium chloride indicated that the following solvolytic reactions had taken place:



and

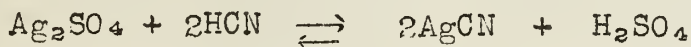


Neither thionyl cyanochloride or the thionyl cyanide could be isolated from the reaction mixture; both decompose rapidly.

B. Solvolysis of Salts. A study of the solvolysis of a series of silver salts was undertaken to establish the relative strength of the parent acids. The silver cyanide formed by such a reaction is insoluble and constitutes a weak base analogue. The following salts are arranged in order of decreasing strength of the parent acid.

AgClO₄. The readily soluble silver perchlorate does not solvolyze and its solutions are good conductors. Silver perchlorate can be used as a qualitative test reagent for the presence of moisture in liquid HCN since it reacts immediately with water to give the insoluble silver cyanide and perchloric acid.

Ag₂SO₄. Silver sulfate reacts as follows:



The presence of sulfuric acid in the supernate liquid was verified by titration with potassium cyanide solution and actual isolation of potassium sulfate.

AgNO₃. Silver nitrate reacts according to the following equation: $AgNO_3 + HCN \rightleftharpoons AgCN + HNO_3$. Conductance studies and potentiometric titrations indicate that the position of the equilibrium is not too far to the right.

Ag₃PO₄. Silver orthophosphate is converted to silver cyanide and orthophosphoric acid when dissolved in HCN. Analysis shows that this reaction is practically quantitative. Conductometric and potentiometric titration of the supernatant phosphoric and solutions show that it is non-basic in liquid HCN.

Jander suggests that the solvolysis of silver orthophosphate in liquid HCN be used as method for preparing anhydrous orthophosphoric acid.

Dear Sir,

I have the honor to acknowledge the receipt of your letter of the 10th inst.

Yours faithfully,

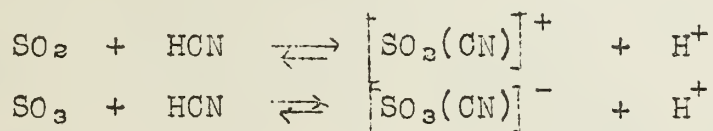
AgOCN. Silver cyanate is insoluble in liquid HCN. After a reaction period of four days at room temperature 42% conversion to silver cyanide was found to have occurred.

It should be noted that potassium cyanate is very soluble in HCN and that these solutions tend to turn brown and resinify--indicating the presence of free cyanide ions. Complete solvolysis occurs but no free cyanic acid could be detected. Jander (14) states that cyanic acid is the hydrogen peroxide analogue of the cyano system and that it readily decomposes to hydrogen cyanide and oxygen. However, all tests for oxygen were negative.

AgI. Silver iodide does not solvolyze. These results show that solvolysis of the silver salts depends upon initial solubility as well as the strength of the acid analogue.

VI. Reactions of Sulfur Dioxide and Sulfur Trioxide with HCN. Since these two sulfur compounds are the acid anhydrides of sulfurous and sulfuric acids in the aquo system, a study was made to determine their chemical behavior in the cyano-system.

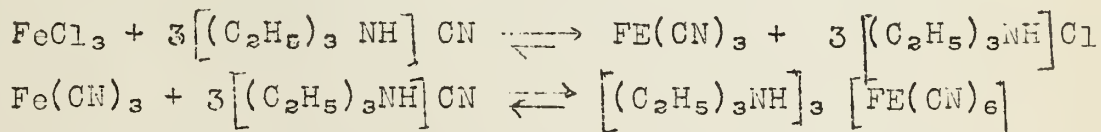
Solutions of sulfur-dioxide and sulfur trioxide in HCN are weak electrolytes; potentiometric titrations with potassium cyanide showed the presence of the mono basic ~~and~~ cyanosulfurous and cyanosulfuric acids, which were formed by the following reactions with the solvent.



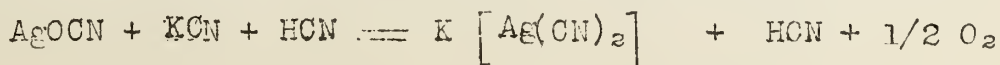
Both of these acids as well as their potassium salts are stable only in solution.

VII. Amphoterism or Complex Formation. Since the salts of iron, platinum, gold, silver, copper, cadmium, nickel, cobalt, and mercury exhibit a marked tendency to form complex cyanides in the aquo system, it was of interest to determine whether some of these same compounds would act as amphoteric cyanides in liquid HCN. The following examples are discussed in the most recent work by Jander (16).

FeCl₃. Potentiometric titrations of this compound with triethylamine and isolation of the complex triethyl-ammonium hexacyanoferrate (III) indicate the following reaction sequence:



AgCN. The insoluble silver cyanide readily complexes with an additional mole of either potassium or triethylammonium cyanido-triethyl amine in liquid HCN - to yield the dicyanoargentate ion. Silver perchlorate, and silver iodide can be converted readily to the insoluble silver cyanide and then to the soluble complex by metathetical reactions. Silver cyanate complexes as follows:



$\text{Hg}(\text{CN})_2$. This compound is slightly soluble in liquid HCN. Reaction with one or two moles of potassium cyanide yields potassium tricyanomercuriate (II) and potassium tetracyanomercuriate (II). Mercury (II) chloride can be converted by metathesis to either of these complexes.

VIII. Solvation. Liquid HCN has little tendency to form solvation compounds in spite of the fact that it possesses a high dielectric constant.

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METALLURGY OF TITANIUM

Robert J. Peavler

April 12, 1949

Introduction:

Titanium compounds have been used in large quantities in recent years, but metallic titanium has been almost unknown because of the difficulty of obtaining the free element. It has been estimated that titanium makes up about 0.63% of the earth's crust, being about as abundant as chlorine, and many times more plentiful than such more familiar metals as copper and lead (1). Of the metals suitable for structural use, it is exceeded in abundance only by aluminum, iron and magnesium. Although sodium, potassium and calcium are more plentiful than titanium, they are not suited for use as structural materials.

History:

Titanium was identified as a new element by Gregor in 1789, but not until a hundred years later was the free element prepared, and then only in an impure state (2). Several workers, including Berzelius, claimed to have obtained free titanium, but it now seems likely that the products obtained were carbides or nitrides, which frequently are metallic in appearance (3). Moissan (4), using the high temperature of the electric furnace, obtained titanium which contained a considerable amount of the carbide, TiC , and Nilson and Petersson (5) obtained titanium about 95% pure by reducing the tetrachloride with sodium. Because of the lack of purity of the product, it was generally believed that titanium is a brittle, unworkable metal. It was not until Hunter (3) succeeded in preparing titanium in a nearly pure state that its malleable properties were recognized. In 1940, Kroll (6) developed a process for reducing titanium tetrachloride with magnesium; this process is now used technically. No electrolytic process has, therefore, been developed.

Titanium Ores:

The two principle ores of titanium are rutile, TiO_2 , and ilmenite, essentially $FeTiO_3$ with variable amounts of iron. Because of the great abundance of rutile sands in Australia, rutile is the principal source of titanium in that country (7); in the United States, the greater abundance of ilmenite and its more ready workability make it the principal source of titanium (8). Greatest production of ilmenite in the United States occurs in the Adirondack region of New York, but large deposits are also being worked in Florida, North Carolina and Colorado. American ilmenite generally contains from 44 to 50 per cent titanium dioxide.

The preparation of titanium (IV) chloride used in the Kroll process from ilmenite is complicated by the great amount of iron present; however, ilmenite is generally preferred over rutile as a source of titanium whenever it is easily obtained, since rutile is difficult to process. The titanium is converted into titanium tetrachloride by the use of carbon and chlorine, and the crude tetrachloride is purified by distillation and treatment with copper. Pure titanium (IV) chloride is a colorless liquid. (9)

Production of metallic titanium:

Practically all titanium which is now being produced is obtained by some modification of the Kroll process, involving the reduction of the tetrachloride by magnesium.



Titanium oxide cannot be used because complete reduction cannot be accomplished (10), and the presence of very small amounts of oxide is sufficient to completely destroy all ductile and malleable properties of the resulting product.

In the process as used by the Bureau of Mines (19), the reduction is carried out in a closed iron vessel at a temperature of 1475° to 1650° F. Since oxygen or nitrogen must not be present, an atmosphere of helium is maintained in the vessel. An excess of magnesium must be present in order to avoid the formation of lower chlorides of titanium.

In the removal of magnesium chloride and excess magnesium, two methods have been used:

- 1) The spongy product is drilled out of the reaction vessel with a lathe, the chips then leached with dilute hydrochloric acid, ground and sifted, and the ground material again leached in strong hydrochloric acid, after which it is washed, dried, rescreened and magnetically separated. The product is obtained as a powder.
- 2) Heating the reaction chamber in a vacuum retort, either to volatilize the magnesium and the chloride or to melt their substances so that they can be drained off.

The principle impurities in the product are magnesium, chlorine, manganese and oxygen. Magnesium can be reduced to a negligible amount by vacuum sintering at a high temperature. Chlorine cannot be removed by vacuum sintering, but is removed almost completely by fusion. Iron comes from the walls of the reaction vessel; the amount cannot be decreased by heat treatment, but is decreased by leaching. Manganese is introduced as an impurity in the magnesium; the amount of manganese cannot be decreased by heat treatment or leaching, but it can be avoided by using pure magnesium. Actually, of these impurities only oxygen causes great trouble, and no means of removing it has yet been found. It is likely that much of the oxygen comes from moisture and hydrated magnesium compounds caught in the pore structure of the titanium during leaching.

Hydrogen is adsorbed by the titanium during leaching; while hydrogen causes brittleness, it can be largely removed by heating in a vacuum.

Consolidated Titanium:

The preparation of massive titanium presents great difficulties because of its high melting point, 1730° C, which makes fusion very difficult, so that it cannot easily be cast into large objects. The problem of fusion is further complicated by the great tendency of titanium to react with almost any refractory lining. Alumina, beryllia and silica refractories are useless (11). Metal furnace linings cause trouble because few metals have melting points higher than that of titanium; in addition, alloying with the metal may occur. Titanium has been successfully fused in thoria and graphite crucibles, but an entirely suitable refractory has not yet been found (22,23). Success has also been had by melting titanium in water-cooled crucibles of copper with which titanium does not alloy, and furnaces of such design that the molten metal comes into contact only with titanium powder (24). Induction or electric arc heating is generally employed.

Powder metallurgy presents a satisfactory method of dealing with titanium. If the powdered metal is heated under pressure at temperatures below the melting point, the particles adhere and slow diffusion occurs with the formation of a consolidated mass. However, ordinary methods of powder metallurgy are not easily applied to the fabrication of large objects. One procedure which has been used with success is to seal the powder in iron containers and then rotate the assembly at high temperatures. The amount of titanium which can be worked by this method is almost unlimited (20).

The thermal decomposition process of de Boer and von Arkel has been employed experimentally. (12,13) In this process, the crude titanium is converted into the volatile iodide, TiI_4 , which is then decomposed by an incandescent filament, on which the metal is deposited. A very pure and ductile titanium is produced in this manner, but the amount which can be made by this method is limited. However, considerable work is now being done with this process with a view toward making it commercially feasible (21).

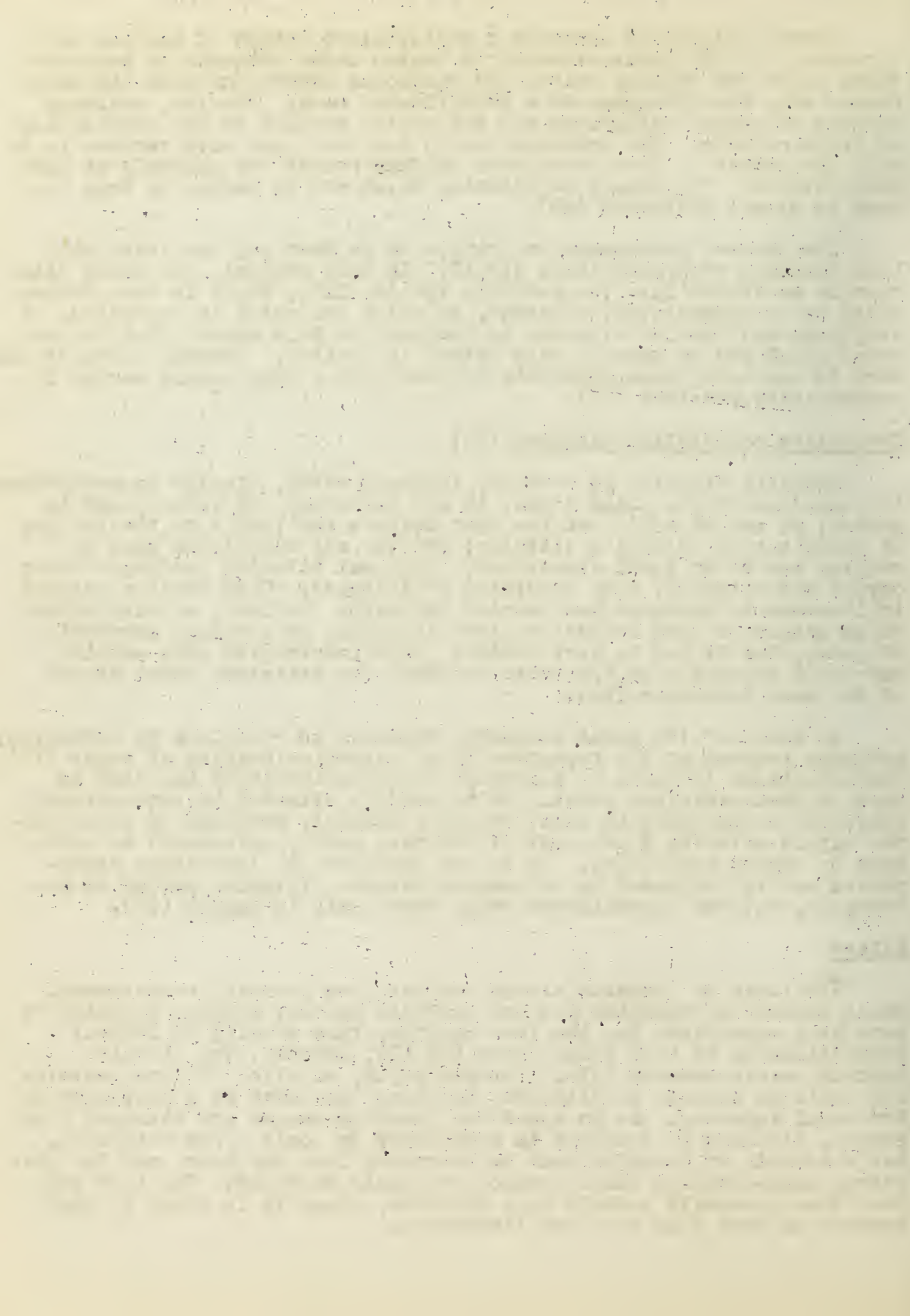
Properties of metallic titanium (14)

Metallic titanium is a white, lustrous metal, similar in appearance to stainless steel. Like steel, it can be forged and rolled, and in general it can be said that the same methods applicable to the forging of steel can be used with titanium; however all operations must be carried out in an inert atmosphere, since hot titanium readily absorbs oxygen and nitrogen, with resulting brittleness. Cold working results in increase in hardness and tensile strength. Ordinary welding procedures cannot be used because of the difficulty of avoiding absorption of gases, but it can be spot welded. Experiments with spot welding show weld strengths of the order of those for stainless steel plates of the same thickness (25).

In spite of its great activity, titanium is resistant to corrosion, probably because of the formation of a protective coating of oxide (14). Investigations indicate a resistance to corrosion about the same as that of 18-8 stainless steel. It is readily attacked by concentrated sulfuric or hydrochloric acid, but only slightly attacked by concentrated nitric acid (by 5 per cent of ordinary acids, solutions) by ammonium or sodium hydroxides. It is not tarnished by laboratory atmospheres and is resistant to salt-spray attack. Titanium powder is pyrophoric, but the consolidated metal burns only in oxygen (15).

Alloys

The field of titanium alloys has not been greatly investigated. Small amounts of titanium are now included in many steels, in which it acts as a stabilizer for the iron carbide, thus tending to inhibit graphitization at high temperature, (16,17); however, the titanium content rarely exceeds 0.1%. Ferrotitanium, an alloy of iron containing variable amounts of titanium, has long been used as a scavenger in the steel industry. As an agent for removing oxygen and nitrogen from steels, titanium is exceeded in efficiency by only a few materials. Large amounts of titanium tend to decompose iron carbides, and for this reason high-titanium steels cannot be easily hardened. Pig iron and cast iron generally contain some titanium, since it is found in small amounts in most iron ores and limestones.



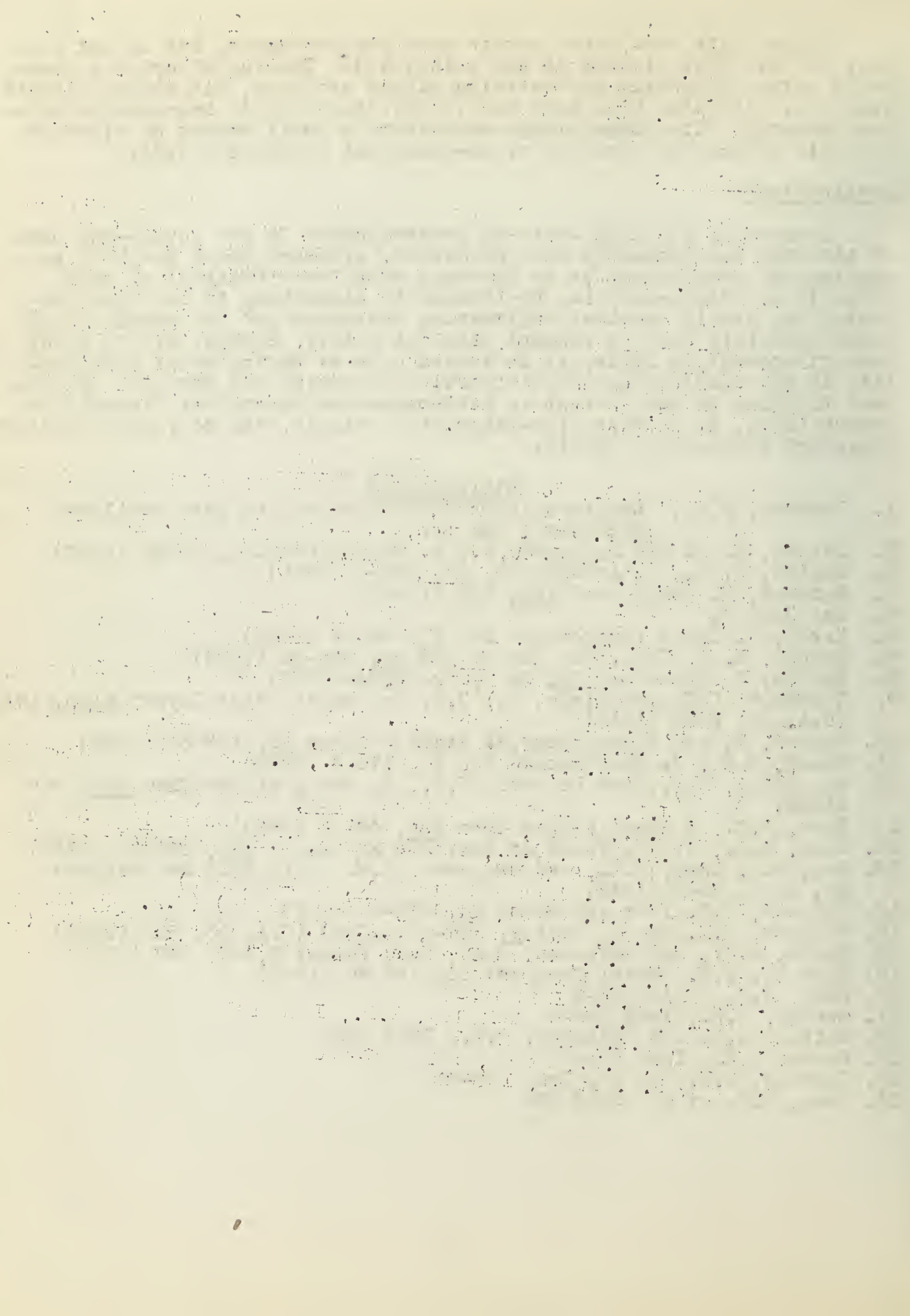
Alloys with some other metals have been prepared, but do not appear to have been studied to any extent (6). Thorium alloys are generally soft. Columbium and tantalum alloys are hard, but are malleable when hot. Alloying with most metals does not seem to increase brittleness greatly. Zinc-base alloys containing a small amount of titanium are said to possess superior creep-resistant properties (18).

Applications:

Because of its high cost--at present about \$5 per pound--few uses of titanium have actually been developed, although there has been no shortage of speculation as to possible uses for a material of such properties. Because of its resistance to corrosion, it has been suggested for use in chemical engineering equipment and for construction where materials come in contact with sea water. Because of its great strength-to-weight ratio, it is looked upon as having great possibilities in the construction of aircraft. (7) During the war, the Germans used titanium to some extent in getters and as functional elements in vacuum tubes, to produce high-temperature steels, and to form corrosion resistant surfaces on steels.

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NITROSYL CHLORIDE AS A SOLVENT AND SOLVATING AGENT

Leona Glen Schafer

April 19, 1949

INTRODUCTION

Preparation

In 1848 Gay Lussac¹⁴ first prepared nitrosyl chloride by the reaction of nitric oxide and chlorine at 15°. Since then this compound has been prepared in a variety of ways depending upon the reaction of chlorine or a chloride with an oxide of nitrogen or with some simple derivative of nitrogen.

The most practical method of preparing large quantities of nitrosyl chloride is by the reaction of nitric oxide and chlorine. More nearly pure nitrosyl chloride may be made by the addition of sodium chloride³⁷ (or hydrogen chloride)s to nitrosyl sulfate. The latter compound may be prepared by slowly passing sulfur dioxide through fuming nitric acid⁵ or by the action of nitrous acid on concentrated sulfuric acid³⁷.

Physical Properties

At -5.8°C⁴⁰ the orange-yellow nitrosyl chloride gas may be condensed to a dark red liquid. Blood-red crystals⁴¹ form at -60° to -61°; upon cooling to liquid air temperatures they become lemon yellow¹⁰.

Many other physical data for nitrosyl chloride have been recorded: its specific gravity at -12.5° is 1.4165¹⁵; its absorption spectrum has been studied both in visible²⁶ and the infra red³. (The conclusion drawn from the latter study is that NOCl is an unsymmetrical molecule); its dipole moment was formed to be 1.83±.01D²¹; its dielectric constant at 12° is 18.2²¹; its viscosity is .00547 poise at -20°.°; its vapor density agrees with the formula NOCl up to 700° but above that it rapidly dissociates until at 985° it is 50% decomposed into nitric oxide and chlorine³⁵.

PROPERTIES AS A SOLVENT AND SOLVATING AGENT.

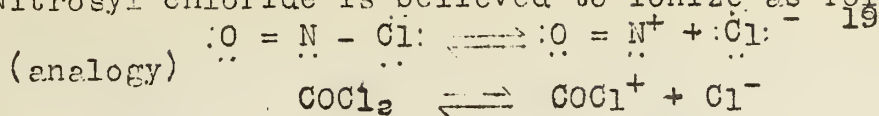
The confusion caused by the various theories of acids and bases is really only a matter of semantics. Whether the word "acid" means (1) a substance which forms hydrogen ions in solution as the only positive ions (Arrhenius); (2) a proton donor (Brønsted); (3) any electrolyte which in a given solvent yields cations identical with the cation of the parent solvent; anions contain in addition to the atom characteristic of the acid, atoms characteristic of the parent solvent (Franklin); or is limited by the four "phenomenological criteria", neutralization, titration with indicators, displacement and catalysis of Lewis²², each definition is consistent with the accompanying theory and can be used satisfactorily.

The Franklin theory as used by Germann, Cady, Jander and others is to be considered in the following discussion of properties of nitrosyl chloride as a solvent.

The requirements of a parent solvent are few. It should (1) be a good solvent, (2) be very slightly ionized, (3) be associated, (4) have a low viscosity, (5) have a high dielectric constant. Since nitrosyl chloride corresponded to these needs fairly well (being comparable to ammonia in the values for 4 and 5 above) Burg and Campbell felt that it would be a "fairly effective ionizing solvent"⁷.

Ionization

Nitrosyl chloride is believed to ionize as follows:



The NO^+ ion should be strongly solvated because of resonance structures $[\ddot{O} = \ddot{N} - \ddot{Cl} - \ddot{N} = \ddot{O}]^+$ $[\ddot{O} = \ddot{N} - \ddot{Cl}]^+ : \ddot{N} = \ddot{O}$ and $:\ddot{O} \equiv N^+[:\ddot{Cl} - \ddot{N} = \ddot{O}:]$. Therefore it might have been expected that nitrosyl compounds, acids in this system, should be soluble in nitrosyl chloride forming solutions having high electrical conductivities. Table I shows that this is true for the mono nitrosyl compounds $NOAlCl_4$, $NOFeCl_4$ + $NOSbCl_6$.

However, less favorable results were obtained with the dinitrosyl compounds. $(NO)_2SnCl_6$ + $(NO)_2TiCl_6$. These compounds and $NOSO_4H$ were quite insoluble and non-conducting. $(NO)_2S_2O_7$, not a true solvo acid, showed slight conductivity which passed slowly through a maximum; see Table II. H_2SO_4 was inert.

TABLE I
CONDUCTANCES IN LIQUID $NOCl$

| Solute | Molarity | Temperature
°C | Specific Cond.
Nhos. | Molar Cond. |
|------------|----------|-------------------|-------------------------|-------------|
| $NOAlCl_4$ | .008 | -20 | 1.17×10^{-2} | 119 |
| $NOAlCl_4$ | .0099 | -20 | 1.34×10^{-3} | 136 |
| $NOFeCl_4$ | .0094 | -21 | 1.26×10^{-3} | 134 |
| $NOFeCl_4$ | .0094 | -44 | 1.00×10^{-3} | 106 |
| $NOSbCl_6$ | .140 | -20 | 2.35×10^{-2} | 168 |
| $NOSbCl_6$ | .140 | -44 | 2.20×10^{-2} | 157 |
| $NOCl$ | pure | -20 | 2.80×10^{-6} | — |

TABLE II
CONDUCTANCE OF $(NO)_2S_2O_7$ (SATURATED IN $NOCl$) AT 20°

| Time (hrs) | 0 | .75 | 2 | 15 | 46 |
|-------------------------------------|------|-----|------|------|------|
| Specific Cond.
($\times 10^6$) | 4.95 | 25 | 48.8 | 23.8 | 14.7 |

The chloride ion was not expected to be appreciably solvated because nitrosyl chloride should not be affected by an electron donor as weak as the chloride ion. To support this potassium chloride was found to be insoluble in nitrosyl chloride; there was no conductance effect.

The choice of KCl is perhaps unfortunate for it is a base in this system and yet; when the acid $NOSbCl_6$ was added it remained unchanged; by analogy it should have dissolved. Perhaps a protective coating of $KSbCl_6$ prevented this.

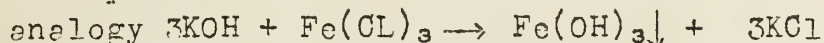
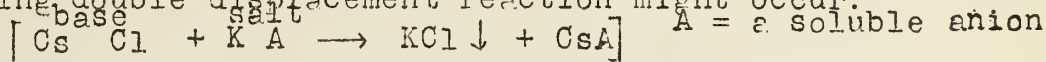
More contradictory evidence was brought up when in an attempt to establish the presence of chloride ions in nitrosyl chloride water was added. Burg and Campbell reported that water dissolved with no conductance and could be recovered by evaporation; however slow hydrolysis at room temperature resulted in the formation of products NO , NO_2 , HCl , also non-conducting in nitrosyl chloride. In 1924, Noyes³⁰ reported the decomposition, $NOCl + H_2O \rightarrow HONO + HCl$

Neutralization.

Since no base (metallic chloride) soluble in nitrosyl chloride has been found the reaction of neutralization remains hypothetical.



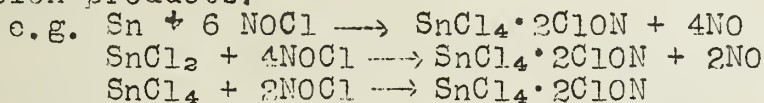
Much work may still be done along this line. Perhaps CsCl would be soluble (as in the case of CS_2SO_3 in liquid SO_2). If so, the following double displacement reaction might occur:



Solvation

Solvates, that is compounds containing solvents of crystallization, such as hydrates, ammonates, phosgenates are common. The solvo- acids, NOAlCl_4 (or $\text{AlCl}_3 \cdot \text{NOCl}$) and NOSbCl_4 (or $\text{SbCl}_3 \cdot \text{NOCl}$) mentioned before are examples of solvated compounds.

Solvates are usually obtained by the interaction of the chlorides and nitrosyl chloride alone or in carbon tetrachloride³². However, most metals, metallic oxides^{2,9,34,36,37}. However, most metals, metallic oxides, or lower valent chlorides³ are attacked to form higher valent chlorides and an oxide of nitrogen. Zn, Hg, Al, Sn, As, Sb, Bi are attacked while cold. Cu, Au, Cd, Th, Pb, Pt are attacked when kept at 100° for many days. Ag, Mn are slightly attacked under the latter conditions. Mg + Ni show no corrosion³³. The higher valent chlorides thus formed usually combine with some of the excess solvent to form molecular addition products.



Mono-solvates are obtained with SbCl_5 , AlCl_3 , FeCl_3 and BiCl_3 . PtCl_4 , SnCl_4 , TiCl_4 , and PbCl_4 form disolvates³².

$\text{ZnCl}_2 \cdot \text{NOCl}$, $\text{AlCl}_3 \cdot \text{NOCl}$ and $\text{HgCl}_2 \cdot \text{NOCl}$ are loose addition compounds from which NOCl may be removed on heating. The compounds $\text{CuCl}_2 \cdot \text{NOCl}$ and $\text{MnCl}_2 \cdot \text{NOCl}$ are paramagnetic and are thus believed to possess the structures represented by the formulas $[\text{CuNO}] \text{Cl}_2$ and $[\text{MnNO}] \text{Cl}_2$. Magnetic evidence also supports the belief that the following compounds are saltlike: $[\text{NO}^+ \text{SbCl}_6]^-$, $2(\text{NO})^+ [\text{SnCl}_6]^-$, and $2(\text{NO})^+ [\text{PtCl}_6]^-$. Some evidence indicates that NOSbCl_6 resonates between a salt and a molecular addition product¹.

Chemical reactivity

"There is probably no known compound which provides a greater variety of reactions compared to the simplicity of its structure and to the resistance shown toward decomposition by physical agencies."⁷

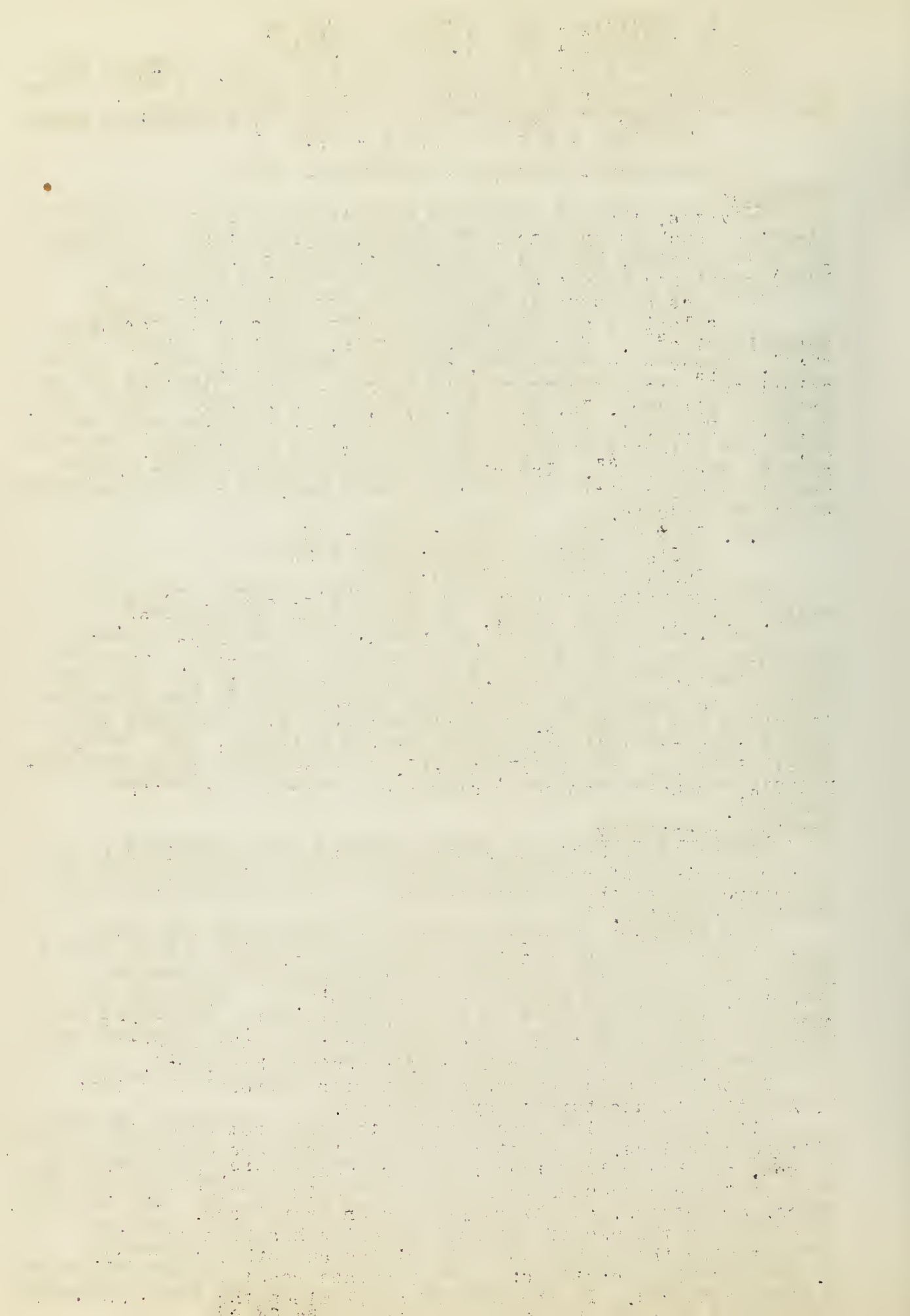
When nitrosyl chloride reacts with bases (in the water system) chlorides and nitrites are formed³¹. $\text{NOCl} + \text{KOH} \rightarrow \text{KCl} + \text{KONO} + \text{H}_2\text{O}$. With hydrogen sulfide in ether ammonium chloride, water, and sulfur are produced¹⁸. Chlorine is miscible with liquid NOCl in all proportions⁴¹. Treatment with hydrogen using a platinum catalyst results in the formation of ammonium chloride and some hydroxylammonium chloride¹⁸.

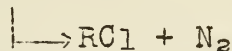
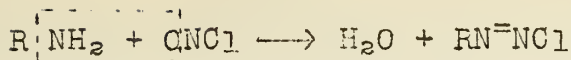
Certain organic compounds react with nitrosyl chloride:

1. Addition to unsaturated hydrocarbons.

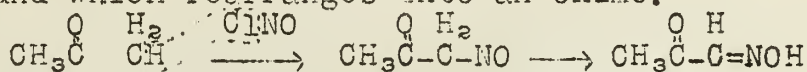
Nitrosyl chloride reacts with ethylenic compounds to form nitroso chlorides. In crystalline form these are colorless dimers; in soln. or when melted they form blue monomers¹². Upon heating, many of these compounds rearrange into oximes which produce aldehydes, or ketones, and hydroxylamine on hydrolyses. The formation of oximes by the use of nitrosyl chloride has been used to characterize the double bonds in pinene and other terpenes.

2. Condensation reactions: Primary amines react to form water and a diazo compound. In the case of alkylamines, the diazo compounds break down to form chlorides and nitrogen^{28,29,39}.

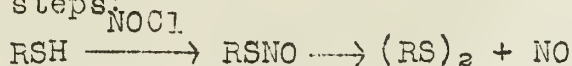




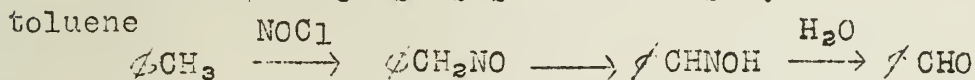
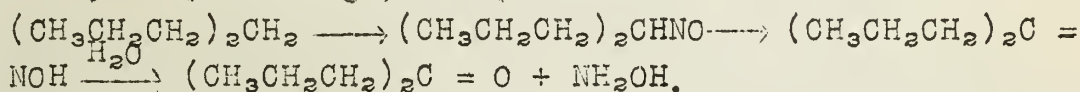
With substituted aryl compounds such as phenol the nitroso group is directed to the para position²⁷. Secondary amines form nitroso amines $R_2NH + NOCl \longrightarrow R_2N.NO + HCl$. Acetone forms a nitroso compound which rearranges into an oxime.



Mercaptans also undergo reaction with NOCl in accordance with the following steps:



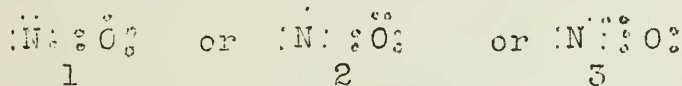
Even paraffins are attacked by nitrosyl chloride^{23,24}. In presence of ultra-violet light, they condense to form nitroso compounds which rearrange to form oximes; the latter yield ketones on hydrolysis: e.g., n-heptane



STRUCTURE

"The nitrosyl grouping is truly an unusual grouping among chemical materials"²⁷. Although it contains an odd number of electrons compounds show little color, and only a slight tendency to dimerize or to ionize at room temperature.

Possible structures for nitric oxide may be represented as follows:



Inter nuclear distances support a resonance structure intermediate between forms 2 + 3. The bond distance in NO is 1.14Å° with 1.18Å° calculated for a double bond, 1.06Å° for a triple bond.

Nitric oxide may react in three ways: 1) through actual or effective loss of an electron, $NO^+(:N=O:)^+$, 2) by the gain of an electron from some electropositive material $NO^-(:N=O:)^-$ 3) by donating a pair of electrons to form a coordination compound, $(:N=O:)$, $(:N=O:)^+$, or $(:N=O:)^-$.

For nitrosyl chloride Ketelaar²⁵ found that the bond distances are : $2.65 \pm .01$ for Cl-O, $1.95 \pm .01$ for Cl-N, + $1.1 \pm .02$ for N-O. The ONCl bond angle is $116^\circ \pm 2$.

The dipole moment for nitrosyl chloride is 1.83D, thus indicating polarity or an unsymmetrical structure. In the addition of nitrosyl chloride to unsaturated hydrocarbons chlorine has a negative charge according to Markownikoff's rule since it goes to the carbon with the least number of hydrogen atoms. The existence of the NO^+ radical is further supported by magnetic measurements on solvated salts (e.g. $2NO^+ SnCl_6^-$).

No experimental evidence to support the contention that NOCl, like HOCl and NO₂Cl exists in electromeric forms was found. The only known compound in which the nitrosyl group seems to be negative is sodium nitrosyl²⁹.

Conclusion

Huge quantities of nitrosyl chloride are produced in the commercial preparation of chlorine by treating salt with nitric acid. Because its production by this method far exceeds its uses the Solvay Process Company, the manufacture is compelled to decompose much of it to form nitric oxide and more chlorine. Increasing amounts of it are being shipped out in special containers and also in the form of an addition product with

ferric chloride⁴ from which the gas may be liberated by heat.

The Dow Chemical Company holds a patent for preparing nitrosyl chloride by the action of nitric oxide on hydrochloric acid in the presence of an oxidizing agent such as nitric acid. The product thus formed is immediately used to chlorinate methane exhaustively and thus form carbon tetrachloride and relatively pure ammonium chloride.

The Solvay Process Company uses large amounts of nitrosyl chloride in a method for producing synthetic detergents⁴³. Some other uses and suggested uses for nitrosyl chloride include shrink proofing wool⁴⁴, flour bleaching,⁴⁵ catalyzing polymerization reactions in petroleum refining⁴⁶, making dye intermediates⁴⁷, a modified method of sulfuric acid manufacture, pickling metals and alloys and digesting cellulosic materials.

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Gunther L. Eichhorn

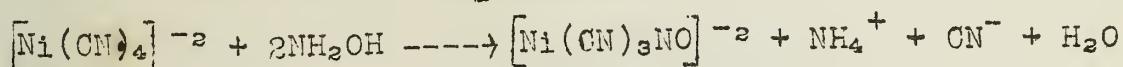
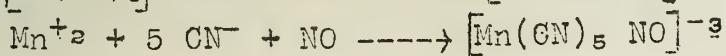
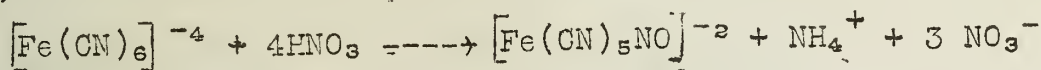
April 26, 1949

Nitrosylcyano Complexes

The nitrosylcyano complexes are isosteric with the metallic carbonyls, and, like the latter, possess a rare gas configuration. Although the initial member of this series, the iron "nitroprussiate," has been known for a long time, the confusion existing in this field has been cleared only recently by the investigations of Hieber and his coworkers.

Preparation:

The compounds to be discussed can be obtained by the action of some nitric oxide source upon the cyanide complex (which may be prepared in the reaction mixture without isolation) corresponding to the nitrosylcyano complex desired. - The source of nitric oxide may consist of an atmosphere of the gas itself, or a reagent such as nitric acid, a nitrite, or hydroxylamine. Following are some typical examples (2,7,10,15):

Structure:

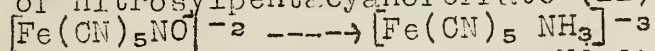
The structural problems pertaining to the nitrosylcyano complexes can be resolved into three fundamental categories:

- 1) the attachment of the NO group to the central atom
- 2) the electronic orbitals utilized in bond formation, and the resultant geometric configuration, and
- 3) the types of bonds connecting metal and coordinating groups.

Our present information concerning the nature of the NO group in these compounds has been summarized by Hieber and Seel (5). Since reduction of the nitrosyl pentacyano ferrate (II) ion leads to the substitution of ammonia rather than water for the NO group (9), the latter is assumed to be joined to the metal through the nitrogen, rather than the oxygen, atom. It remains to be determined whether NO

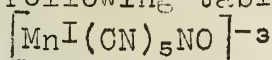
- a) coordinates as a neutral molecule ($\text{Me}-\ddot{\text{N}}\text{O}$)
- b) is a positive ion ($\text{Me}-\text{N}^+=\ddot{\text{O}}$)
- c) is a negative ion ($\text{Me}-\ddot{\text{N}}=\ddot{\text{O}}^-$)
- d) is linked by means of a double bond ($\text{Me}=\text{N}=\ddot{\text{O}}$), or
- e) is an anion of hyponitrous acid $\text{Me}-\text{N}-\ddot{\text{O}}^-$
 $\text{Me}-\ddot{\text{N}}-\ddot{\text{O}}^-$

Structure (a) would impart paramagnetic character, yet all the complexes studied have been found to exhibit diamagnetism. Moreover, the reduction of nitrosylpentacyanoferrate (II)

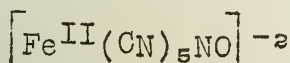


indicates that the charge on the NO differs from that of neutral ammonia. The increase in negative charge of the complex ion, furthermore, provides evidence for structure (b), while simultaneously disproving (c). The latter is all the more unlikely because of a lack of tendency to dimerize, a characteristic of nitroso (but not nitrosyl) compounds. Hieber and Seel consider (d) unlikely, since it postulates a double bond with a transition metal; this objection is no longer valid, on the basis of modern theory. Formula (e) is ruled out by the monomeric nature of 1:1 - metal - to - NO complexes. Thus only structures (b) and (d) are considered logical.

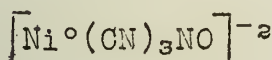
In order to determine which electronic orbitals are used in bond formation, the formal oxidation state of the central atom is first calculated, assuming a charge of +1 for the nitrosyl group and -1 for each of the cyano groups. The electrons which are present (in this oxidation state) in the d-shell being filled in the particular transition series, are then indicated by circles, and the electrons donated by coordinating groups, are represented by crosses. Configurations are presented in the following table, which includes all of the known nitrosylcyano anion



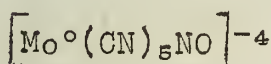
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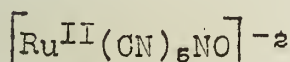
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| o | o | o | x | x | x | x | x | x |



| 3d | | | 4s | | | 4p | | |
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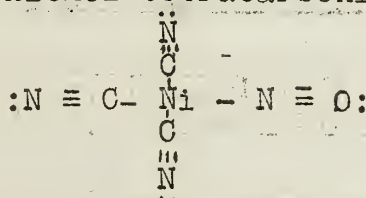
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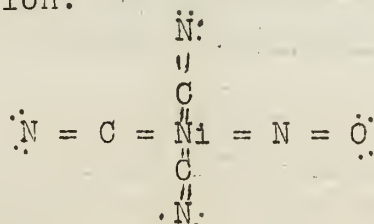
| 4d | | | 5s | | | 5p | | |
|----|---|---|----|---|---|----|---|---|
| o | o | o | x | x | x | x | x | x |
| o | o | o | x | x | x | x | x | x |

The central atom has attained the rare gas configuration in all instances. The nickel complex shows sp^3 bonding, all others utilize $d^2 sp^3$ orbitals; thus, according to Pauling (13), the nitrosyltricyano nickelate (II) ion should be tetrahedral, and all the others should be octahedrally directed. Unfortunately, these predictions have not been experimentally confirmed.

Reference will be made to the nickel complex to illustrate the type of bonding involved in these compounds. Since both the cyanide and the nitrosyl radicals contain ten electrons, the sp^3 configuration closely resembles that of nickel tetracarbonyl:



On the basis of the nickel-carbon distance in nickel carbonyl, Pauling has postulated (13) a double bonded structure as an important contributing element to the resonance of the molecule. By analogy, the nitrosylcyano complex can also be written with four of the 3-d orbitals entering into bond formation:



It appears that these two structures combined yield a satisfactory picture to explain the behavior of the compounds. Many other resonance hybrids can be formulated, including structures in which the central atom is linked by a triple bond (14) to the coordinating groups; since experimental evidence for these possible structures is lacking, we may assume that the contribution of such forms is limited.

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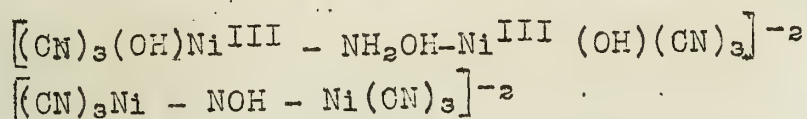
1954

1955

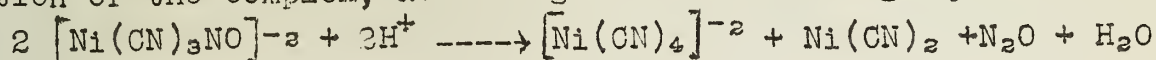
1956

Nitrosyltricyanonickelate (6)

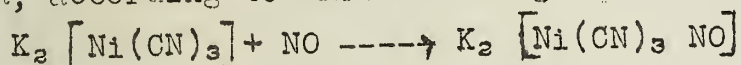
The formation of a violet coloration when potassium tetracyanonickelate (II) is treated with hydroxylamine in aqueous solution or when nitric oxide reacts with potassium tricyano nickelate (I) has been the subject of study by several investigators (1,6,11); conflicting interpretations have been advanced. Thus the following structures, among others, have been proposed for the product:



In order to settle the nature of the violet product, Hieber, Nast, and Proeschel (6) set out to isolate the compound, which they believed to be a nitrosylcyano complex. Anderson (1) had previously attempted the isolation of the $\text{Ni}(\text{CN})_3\text{NO}^{-2}$ anion by precipitation with large cations but no insoluble products were obtained. Hieber *et al* assumed that the compound could not be isolated from aqueous solution due to acid decomposition of the complex, according to the following equation:



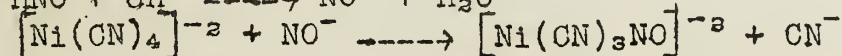
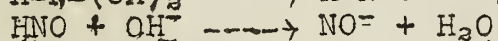
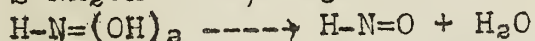
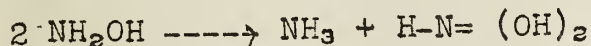
The hydrogen ion concentration furnished by the solvent water is apparently high enough to bring about this reaction. Assuming this hypothesis to be correct it should be possible to isolate the compound from a solvent with a lower acid dissociation constant than water. The successful application of this concept resulted in the isolation of the desired substance both from liquid ammonia and from absolute alcohol media, according to the following equation:



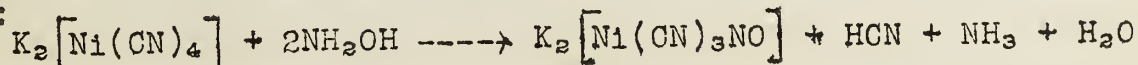
Separation from the side reaction products is effected by extraction with alcohol and ether. Hieber's claim to the effect that they had isolated the only Ni (0) compound other than nickel tetracarbonyl is challenged by the description in the literature of potassium tetracyanonickelate (0). (3,4).

Mechanism of the Reaction with Hydroxylamine

Since the reaction between hydroxylamine and potassium tetracyanonickelate (II) is carried out in aqueous alkaline solution, the violet reaction product could not be isolated. It was proved identical with the substance produced in liquid ammonia by absorption spectra studies (7). The mechanism of this reaction was then formulated, as follows:



Summation of the four steps gives the overall stoichiometric relationship:



Some proof for this mechanism was afforded by the quantitative determination of ammonia produced, and by a variation of the procedure, in which other substances capable of yielding the nitroxyl intermediate were substituted for hydroxylamine.

$$[a_1, a_2, \dots, a_n] = \frac{1}{n!} \det \begin{pmatrix} a_1 & a_2 & \dots & a_n \\ a_1^2 & a_2^2 & \dots & a_n^2 \\ \vdots & \vdots & \ddots & \vdots \\ a_1^{n-1} & a_2^{n-1} & \dots & a_n^{n-1} \end{pmatrix}$$

Let $f(x) = x^2 + 1$ and $g(x) = x^2 - 1$. Then $f(x)g(x) = (x^2 + 1)(x^2 - 1) = x^4 - 1$.

$$f(x) = x^2 + 1, g(x) = x^2 - 1$$

$$f(x)g(x) = (x^2 + 1)(x^2 - 1) = x^4 - 1$$

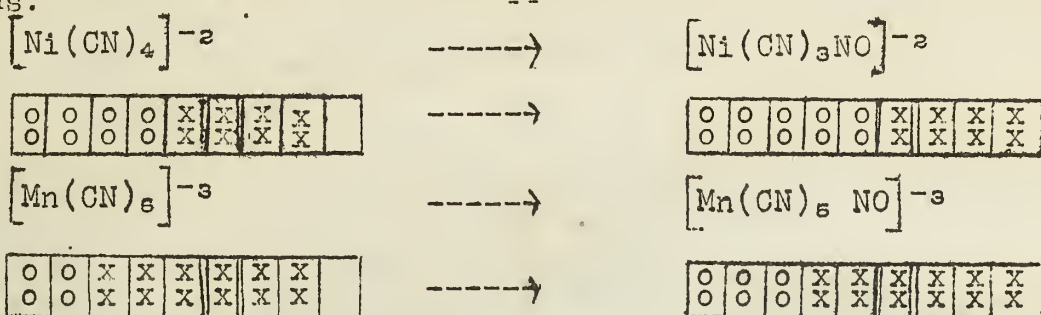
$$f(x)g(x) = x^4 - 1$$

$$f(x)g(x) = x^4 - 1$$

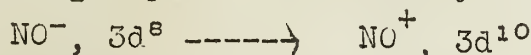
$$f(x)g(x) = x^4 - 1$$

Let $f(x) = x^2 + 1$ and $g(x) = x^2 - 1$. Then $f(x)g(x) = (x^2 + 1)(x^2 - 1) = x^4 - 1$.

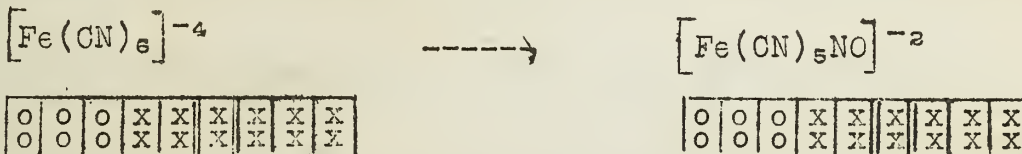
Hexacyanomanganate (III) can be similarly converted to nitrosylpentacyanomanganate (I). (7) Electronically, these reactions can be pictured thus:



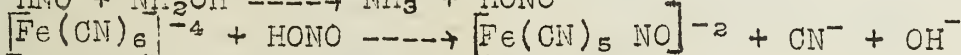
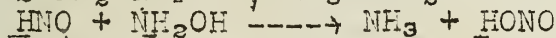
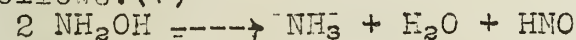
That is, replacement of cyanide by nitrosyl requires the addition of NO as the negative nitroso group, which undergoes an intramolecular reaction with the central atom, in which the latter gains two electrons at the expense of the NO group. Schematically:



It has been determined experimentally that the hexacyanoferrate (II) ion can be converted to the nitroprussiate by hydroxylamine without the addition of alkali. Electronically, the following process is involved:



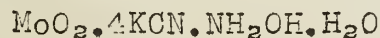
In this particular case, the oxidation state of the central atom remains the same, and the nitroso to nitrosyl reaction apparently does not take place. Therefore we may assume that, in this case, NO adds as a nitrosyl, and not as a nitroso group; the process can be summarized as follows: (7)



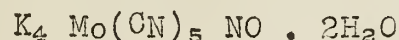
This mechanism explains the fact that no addition of base is necessary and also justifies the direct reaction of nitrite with hexacyanoferrate (II) to give the nitroprussiate. The latter reaction, as may be expected because of the similarity of configuration of reagent and product, is readily reversible (6).

Potassium Nitrosylpentacyanomolybdate (0)

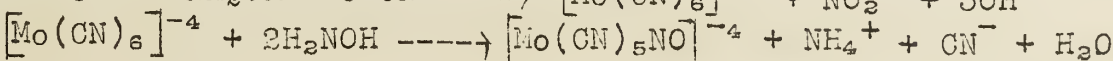
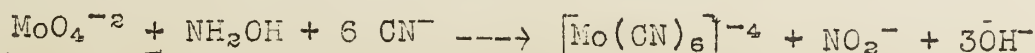
In the older literature a violet, crystalline compound designated as



is described, which was prepared from potassium molybdate, potassium cyanide, and hydroxylamine. In the belief that this is actually another nitrosylcyano complex, Hieber, Nast, and Gehring repeated this work (3) and by analysis, substantiated the formula



Apparently hydroxylamine serves as a reducing agent, as well as nitrosylating agent.



SECRET

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1. The first part of the paper is devoted to a review of the literature on the topic.

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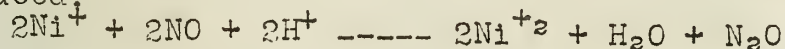
1990

Nitric Oxide Analysis -- Oxidation State of Central Atom

The reaction of nitrosyltricyanonickelate (O) ion with acid has been discussed above. The oxidation of Ni(O) to Ni (II) can be considered in two steps (6), the first involving the reduction of nitrosyl to nitric oxide



and the second representing the further reduction of the nitric oxide produced:



Since the reaction of nitrosylpentacyanoferrate (II) involves only the oxidation from iron (II) to iron (III), no further reduction of nitric oxide takes place, and the reaction in this case, can be used for the quantitative determination of NO in the complex. Whether nitric oxide or its reduction products, nitrous oxide and nitrogen, are evolved on acid treatment thus depends essentially upon the oxidation state of the central atom. In the reaction with the nickel complex further reduction of the nitric oxide can be prevented by the addition of ferric ion, thus enabling the quantitative detection of NO in this complex also.

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19. *Chrysomelidae* (continued)

1990

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1. The first step in the process of the formation of the state is the creation of a common identity among the people. This is achieved through the establishment of a common language, culture, and religion. The second step is the creation of a common territory, which is achieved through the establishment of a common border and a common capital. The third step is the creation of a common government, which is achieved through the establishment of a common constitution and a common set of laws. The fourth step is the creation of a common economy, which is achieved through the establishment of a common currency and a common set of economic policies. The fifth step is the creation of a common social system, which is achieved through the establishment of a common set of social norms and a common set of social services. The sixth step is the creation of a common foreign policy, which is achieved through the establishment of a common set of foreign relations and a common set of international agreements. The seventh step is the creation of a common defense system, which is achieved through the establishment of a common set of military forces and a common set of defense policies. The eighth step is the creation of a common justice system, which is achieved through the establishment of a common set of courts and a common set of legal principles. The ninth step is the creation of a common education system, which is achieved through the establishment of a common set of schools and a common set of educational standards. The tenth step is the creation of a common health system, which is achieved through the establishment of a common set of hospitals and a common set of health policies. The eleventh step is the creation of a common environment, which is achieved through the establishment of a common set of environmental laws and a common set of environmental policies. The twelfth step is the creation of a common culture, which is achieved through the establishment of a common set of cultural institutions and a common set of cultural policies. The thirteenth step is the creation of a common religion, which is achieved through the establishment of a common set of religious institutions and a common set of religious policies. The fourteenth step is the creation of a common language, which is achieved through the establishment of a common set of linguistic institutions and a common set of linguistic policies. The fifteenth step is the creation of a common identity, which is achieved through the establishment of a common set of identity institutions and a common set of identity policies.

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CARBON¹⁴, ITS PREPARATION, PROPERTIES, AND USES

William F. Loranger

May 3, 1949

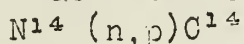
INTRODUCTION:

Perhaps the first consideration in working with a radioactive element is the health hazard involved. Carbon-14 (hot carbon, as it is often called) is a very weak beta-emitter, and as such can penetrate only the thinnest of barriers, less than a few milligrams/cm.² (1). No danger is connected with mere handling of the material in closed containers. The greatest danger lies in the possible ingestion of the isotope in some form or another. Even this is not very dangerous in spite of the long life of C-14, because of the rapid turnover of carbon compounds in the living organism. However, the hard tissues are transformed very slowly, and if as much as 30 microcuries of radioactive carbon are evenly distributed in the bones of an individual of average size, he will receive the maximum daily dose of radiation, 0.1 r/day of radiation (1). As a prevention to ingestion, working under closed systems is safety enough.

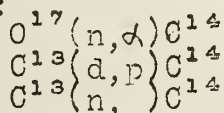
PREPARATION:

There is some evidence of carbon-14 in nature. Cosmic radiations produce a very small amount of it, approximately an abundance of $10^{-10}\%$ C-14 relative to ordinary carbon as 100% (1).

Artificially, radioactive carbon-14 is produced most commonly by means of a cyclotron or a pile such as that in the Clinton Laboratories. When the appearance of protons was observed in the bombardment of N-14 with fast neutrons, the reaction



was suggested as a possibility. Later, the same reaction, evidently, was observed when slow neutrons were used. In a search for the isotopic carbon-14, Ruben and Kamen (4) were able to isolate it and identify it from a graphite rod. These same investigators also isolated it from NH_4NO_3 solutions which received stray neutron radiation for several months from a 30-inch cyclotron. Other reactions observed and utilized by the same men for the production of carbon-14:



The development of nuclear reactors has therefore made possible comparative large-scale production of C-14 of very high specific activity by the neutron bombardment of nitrogenous substances.

Current production of the isotope for distribution is by irradiation of saturated ammonium nitrate solutions in the Clinton Pile (1). From the table below, it is readily seen that the greatest percentage of total activity (60%) is obtained as CO_2 , which is then used to synthesize solid barium carbonate. It is in this form that the activity from such sources is usually obtained by the investigator interested in C-14.

TABLE I. (1)

RADIOACTIVE CARBON COMPOUNDS PRODUCED BY THE REACTION: $N^{14}(n,p)C^{14}$

| Active Body | Target substance -- percentage of total activity | | | | | |
|--------------------|--|---------------------|-----------------------------|-------------------------|--------------|--|
| | Be_3N_2
solid | NH_4NO_3
solid | NH_4NO_3
sat.
soln. | H_2NCH_2COOH
solid | H_2NCONH_2 | $N_2H_4 \cdot 2HCl$
moist
crystals |
| CO | 0.9 | 20 | 30 | 0 | 5 | 10 |
| CH ₄ | 63.0 | 0 | <.1 | 0 | 0 | 5 |
| CO ₂ | 3.3 | 30 | 60 | 10 | 40 | 20 |
| CN ⁻ | 3.5 | 0 | <.1 | 15 | 55 | 70 |
| HCHO | <.01 | 0 | 1 | 0 | 0 | 0 |
| CH ₃ OH | >1.0 | 0 | 1 | 50 | 0 | 0 |
| HCOOH | >16.0 | 0 | 10 | 30 | 0 | 0 |

Looking again at the table, it is interesting to note the large percentage of methane produced from the irradiation of beryllium nitride. This is important because its synthesis from the dioxide is rather time consuming.

PROPERTIES:

The half-life of C-14 has been the subject of numerous investigations, because the beta disintegration of this isotope probably proceeds through a forbidden transition -- the observed half life being much longer than that which one would expect, knowing the maximum beta particle energy to be only about 0.15 mev. (1). Kamen (5) early estimated from 1000 to 25,000 years for its half life. Later experiments on known samples of C-14 content, have given the following values: (1)

5300 \pm 800 years
5100 \pm 200 years
4700 \pm 500 years

Ruben and Kamen (4) have quoted a figure of 0.145 \pm .015 mev. for the maximum beta particle energy.

The physical properties of carbon-14 are best summed up in tabular form, as in the table below, comparing it with the other isotopes of carbon.

TABLE II. (1)
PROPERTIES OF THE CARBON NUCLIDES

| | Abundance | Exact mass
O=16.000000 | Radiation | Max. En-
ergy, mev. | Half-
life | Usual
od'n. |
|-----------------|-------------------|---------------------------|-----------|------------------------|---------------|----------------|
| C ¹⁰ | ... | 10.0210 \pm
.0003 | β^+ | 3.4 \pm 0.1 | 8.3
sec. | B(p,n) |
| C ¹¹ | ... | 11.01495 \pm
.00009 | β^+ | 0.98 \pm .01 | 20.5
min. | B(p,n) |
| C ¹² | 98.9 | 12.00382 \pm
.00004 | | | | |
| C ¹³ | 1.1 | 13.00751 \pm
.00010 | | | | |
| C ¹⁴ | 10 ⁻¹⁰ | 14.00767 \pm
.00005 | β^- | 0.154 \pm
.004 | 5100
yrs. | N(n,n') |

Experimental determinations of the rates of decay of radioactive substances have shown that these processes take place according to an exponential law, the rate of decay at any instant being proportional to the number of unstable nuclei present. The fundamental relation is (6)

$$\frac{dN}{dt} = -\lambda N$$

Integration of this equation gives

$$N_t = N_0 e^{-\lambda t}$$

where N_0 is the original number of unstable nuclei ($t=0$), N_t is the number present after a time t , and λ is the disintegration constant. The time $1/\lambda$ is that necessary for an active deposit to decay to $1/e$ its original strength, and is known as the average life. It is of course now more common to speak of the half life of an active body, the time required for the radioactivity from a deposit to fall to one half its original intensity, being equal to $(\ln 2)/\lambda$.

The long half life of C-14 then as a beta emitter makes it a useful tool for tracer chemistry (3). Some of the methods used to measure this activity in tracer experiments are various forms and adaptations of electroscopes and electrometers. Today, the Lauritzen electroscope and modifications of this is in wide use to measure the radioactivity of gaseous samples. The Lindemann electrometer was and is used for astronomical observations. There are also many "tube counters" in use, of which the Geiger-Müller counters are in popular use. Other measuring devices in use are the Wilson cloud chamber, the beta ray spectrometer, and the mass spectrograph (1, 2, and 12).

Because of their relatively high specific charge, beta rays are quite easily deflected from their paths. This gives rise to "scattering." This is an important consideration in that it considerably weakens the beta ray beams, and experimentally observed absorption curves include this error.

Carbon-14, in the emission of beta particles, also offers the problem of self-absorption of those particles to give inaccurate results. Correction curves are usually plotted (10) to combat this error. Leslie (11) did much experimentation on this important factor, as did Yenkwich (9, 10). It should also be pointed out that active barium carbonate has the property of losing some of its radioactivity through an exchange reaction with atmospheric CO_2 , through the agency of moisture (12).

USES:

Tracer chemistry is important in the use of the radioactive isotopes such as C-14 to "trace" or "follow" the path of a reaction, or what is now more commonly called the "mechanism" of a reaction. By synthesizing with C-14 and tracing its path in the synthesis with suitable counting techniques, some picture of the mechanism is obtained. For example, the work of Kummer, DeWitt and Emmett (13) on the studies of the Fischer-Tropsch synthesis using C-14 as a tracer show that the greater part of the product of synthesis is formed by some process other than by the reduction of the carbide as an intermediate. (This mechanism of carbiding is proposed in Gilman, p. 791).

Probably the most dramatic employment of carbon-14 is in the great amount of research being carried on in attempts to trace the path of carbon in photosynthesis. This is done by the determination of labelled carbon atoms in the intermediates involved (14). This process consists in feeding a photosynthesizing organism radioactive carbon dioxide for various lengths of time

and stopping the reaction by killing the plant. Families of curves are then plotted depicting increases in radioactivity in each compound as a function of time (15). Experimentation is still going on toward these ends.

"in vivo" experiments have been begun, lately, involving the use of carbon-14, with particular reference to the role of CO_2 in the individual blood cells (16).

An interesting experiment carried out by Leifer, Roth and Hempleman (17) was one in which they tried to determine the fate of the carbon in the urea molecule in metabolism. C-14 labeled urea was synthesized and the gross metabolism was studied in a series of mice.

CONCLUSION:

It is interesting to note that in the twelve month period prior to July 31, 1947, nearly 100 shipments of carbon-14 were made to various places in the United States for experimental use. (as compared to 201 for phosphorous-32, 313 for iodine-131, and 22 for sulfur-35.) This is evidence of the increasing importance of carbon-14 as a radioactive tracer. The importance of the isotopes of phosphorous and iodine has long been known. These isotopes have been used in medical diagnosis and therapy in connection with hyperthyroid conditions and cancers. It is believed that carbon-14 will soon rival these two in work on fundamental metabolism researches, along with expanding fields of research in tracing mechanisms of inorganic and organic reactions.

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THE STABILITY OF METAL CHELATES

Allen D. Gott

May 3, 1949

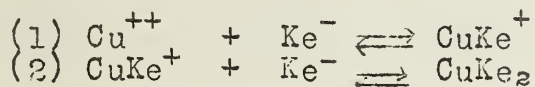
Introduction:

In 1945, Calvin and Wilson (1) studied the influence of the structural factors of organic residues on the stability of chelate compounds. They studied the stability of chelate compounds of divalent copper in which the four atoms bound to the copper were all atoms of oxygen. The cupric ion was chosen in preference to either the cobaltous or ferrous ions since the latter are subject to further oxidation.

The equilibrium was originally represented by the following expression: $\text{Cu}^{++} + 2 \text{Ke}^- \rightleftharpoons \text{CuKe}_2$ (1). The chelating anion in this case was either a β -diketone such as acetyl acetone or an O-hydroxy aromatic aldehyde.

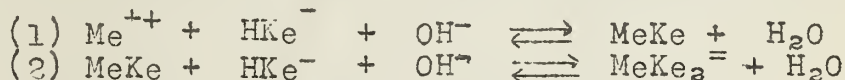
From the known acid dissociation constants of the chelating substances, the known concentration of copper and of chelating substance, and the determination of the hydrogen ion concentration of the solution, Calvin and Wilson (1) attempted to calculate equilibrium constants for the reaction occurring according to the above equation.

The lack of constancy of the calculated equilibrium constants led to the assumption that the reaction occurs in two steps:



wherein the total amount of copper is present as Cu^{++} , CuKe^+ and CuKe_2 and not just as Cu^{++} and CuKe_2 as was originally supposed.

Using the method of J. Bjerrum (2), equilibrium constants for reactions (1) and (2) above were calculated from a knowledge of the average number of chelating anions bound to each cupric ion. The average number of chelating anions is equivalent to the total amount of bound chelating ions divided by the total amount of copper present. The total amount of chelating ion combined with the copper may be calculated from various appropriate equations but is more easily determined graphically. If aqueous sodium hydroxide is used in titration to determine the acid concentration of the solution, which contains a dibasic organic acid anion such as the 5-salicylaldehyde sulfonate ion, the reaction may be thought of as proceeding according to the expressions: (3)



If the pH of the solution, as determined by a pH meter, is plotted against the number of milliliters of sodium hydroxide added, both before and after the addition of the metal ion, the difference in the curves measures accurately enough the total number of moles of chelating ion bound to the metal cation (3).

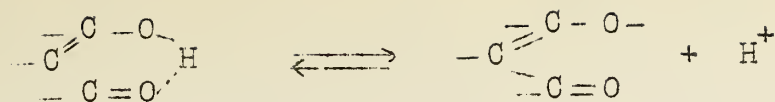
Bjerrum (2) has shown that when the average number of Ke^- bound to a metal ion equals 0.5, then $1/(\text{Ke}^-) \approx k_1$; when it equals 1.5, $(1/\text{Ke}^-) \approx k_2$; and when it equals 1.0, $(1/\text{Ke}^-)^2 \approx K = k_1 k_2$.

Structure:

Calvin and Wilson (1) compared the constants for acid dissociation, which can be expressed as,

1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100. 101. 102. 103. 104. 105. 106. 107. 108. 109. 110. 111. 112. 113. 114. 115. 116. 117. 118. 119. 120. 121. 122. 123. 124. 125. 126. 127. 128. 129. 130. 131. 132. 133. 134. 135. 136. 137. 138. 139. 140. 141. 142. 143. 144. 145. 146. 147. 148. 149. 150. 151. 152. 153. 154. 155. 156. 157. 158. 159. 160. 161. 162. 163. 164. 165. 166. 167. 168. 169. 170. 171. 172. 173. 174. 175. 176. 177. 178. 179. 180. 181. 182. 183. 184. 185. 186. 187. 188. 189. 190. 191. 192. 193. 194. 195. 196. 197. 198. 199. 200. 201. 202. 203. 204. 205. 206. 207. 208. 209. 210. 211. 212. 213. 214. 215. 216. 217. 218. 219. 220. 221. 222. 223. 224. 225. 226. 227. 228. 229. 230. 231. 232. 233. 234. 235. 236. 237. 238. 239. 240. 241. 242. 243. 244. 245. 246. 247. 248. 249. 250. 251. 252. 253. 254. 255. 256. 257. 258. 259. 260. 261. 262. 263. 264. 265. 266. 267. 268. 269. 270. 271. 272. 273. 274. 275. 276. 277. 278. 279. 280. 281. 282. 283. 284. 285. 286. 287. 288. 289. 290. 291. 292. 293. 294. 295. 296. 297. 298. 299. 300. 301. 302. 303. 304. 305. 306. 307. 308. 309. 310. 311. 312. 313. 314. 315. 316. 317. 318. 319. 320. 321. 322. 323. 324. 325. 326. 327. 328. 329. 330. 331. 332. 333. 334. 335. 336. 337. 338. 339. 340. 341. 342. 343. 344. 345. 346. 347. 348. 349. 350. 351. 352. 353. 354. 355. 356. 357. 358. 359. 360. 361. 362. 363. 364. 365. 366. 367. 368. 369. 370. 371. 372. 373. 374. 375. 376. 377. 378. 379. 380. 381. 382. 383. 384. 385. 386. 387. 388. 389. 390. 391. 392. 393. 394. 395. 396. 397. 398. 399. 400. 401. 402. 403. 404. 405. 406. 407. 408. 409. 410. 411. 412. 413. 414. 415. 416. 417. 418. 419. 420. 421. 422. 423. 424. 425. 426. 427. 428. 429. 430. 431. 432. 433. 434. 435. 436. 437. 438. 439. 440. 441. 442. 443. 444. 445. 446. 447. 448. 449. 450. 451. 452. 453. 454. 455. 456. 457. 458. 459. 460. 461. 462. 463. 464. 465. 466. 467. 468. 469. 470. 471. 472. 473. 474. 475. 476. 477. 478. 479. 480. 481. 482. 483. 484. 485. 486. 487. 488. 489. 490. 491. 492. 493. 494. 495. 496. 497. 498. 499. 500. 501. 502. 503. 504. 505. 506. 507. 508. 509. 510. 511. 512. 513. 514. 515. 516. 517. 518. 519. 520. 521. 522. 523. 524. 525. 526. 527. 528. 529. 530. 531. 532. 533. 534. 535. 536. 537. 538. 539. 540. 541. 542. 543. 544. 545. 546. 547. 548. 549. 550. 551. 552. 553. 554. 555. 556. 557. 558. 559. 560. 561. 562. 563. 564. 565. 566. 567. 568. 569. 570. 571. 572. 573. 574. 575. 576. 577. 578. 579. 580. 581. 582. 583. 584. 585. 586. 587. 588. 589. 590. 591. 592. 593. 594. 595. 596. 597. 598. 599. 600. 601. 602. 603. 604. 605. 606. 607. 608. 609. 610. 611. 612. 613. 614. 615. 616. 617. 618. 619. 620. 621. 622. 623. 624. 625. 626. 627. 628. 629. 630. 631. 632. 633. 634. 635. 636. 637. 638. 639. 640. 641. 642. 643. 644. 645. 646. 647. 648. 649. 650. 651. 652. 653. 654. 655. 656. 657. 658. 659. 660. 661. 662. 663. 664. 665. 666. 667. 668. 669. 670. 671. 672. 673. 674. 675. 676. 677. 678. 679. 680. 681. 682. 683. 684. 685. 686. 687. 688. 689. 690. 691. 692. 693. 694. 695. 696. 697. 698. 699. 700. 701. 702. 703. 704. 705. 706. 707. 708. 709. 710. 711. 712. 713. 714. 715. 716. 717. 718. 719. 720. 721. 722. 723. 724. 725. 726. 727. 728. 729. 730. 731. 732. 733. 734. 735. 736. 737. 738. 739. 740. 741. 742. 743. 744. 745. 746. 747. 748. 749. 750. 751. 752. 753. 754. 755. 756. 757. 758. 759. 760. 761. 762. 763. 764. 765. 766. 767. 768. 769. 770. 771. 772. 773. 774. 775. 776. 777. 778. 779. 780. 781. 782. 783. 784. 785. 786. 787. 788. 789. 790. 791. 792. 793. 794. 795. 796. 797. 798. 799. 800. 801. 802. 803. 804. 805. 806. 807. 808. 809. 810. 811. 812. 813. 814. 815. 816. 817. 818. 819. 820. 821. 822. 823. 824. 825. 826. 827. 828. 829. 830. 831. 832. 833. 834. 835. 836. 837. 838. 839. 840. 84

1. The first part of the paper is devoted to a review of the literature on the topic.



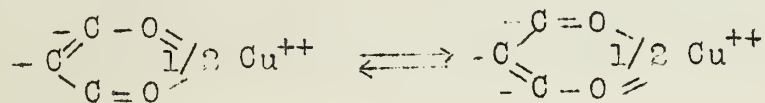
and the constants for the chelation of the above type anion, which can be expressed as,



which appears antithetical to the first expression. They found that there were two forces at work in the chelation of metal ions, (1) one similar to that of hydrogen chelate bonding but the other differing and depending on the structure of the organic anion.

It was apparent that the most profound change was in the nature of the double bond between the two carbon atoms of the three carbon system forming the conjugated chain between the two oxygen atoms. Using Pauling's system (4) a number was assigned to various organic anions, which expressed the degree of "double-bondedness" of the bond between two of these three carbon atoms, forming a resonating system other than the enolate type. It was found that the decrease in "double-bondedness" was the same as the order of decreasing enolate resonance and also the same as the order of decreasing stability of the copper chelate compounds (1).

The preferable answer to the effect mentioned would be to write as an important contribution a completely conjugated six-membered ring in the following manner: (1)



Such structures would involve the availability and geometry of orbitals of the metals and it was in this connection that Calvin and Melchior (3) recently investigated the effects of various metal ions on the stability of chelate compounds in order to obtain an explanation of the part played by the metal ion orbitals in formulation of such structures as suggested above.

Stability and Electronic Configuration:

Calvin and Melchior determined the chelate stability constants of the 5-salicylaldehydesulfonate ion with the divalent ions of copper, nickel, cobalt, and zinc, using the method of Bjerrum (2) already mentioned.

It was found that the stabilities decreased in the order of Cu^{++} , Ni^{++} , Co^{++} , and Zn^{++} . An attempt was next made to relate the above order to the order of such values as decreasing ionic radius, heat of hydration, partial molal entropy, and both the first and second ionization potentials (5). The only possible correlation was with the second ionization potentials which for $\text{Cu} = 20.2$ volts, $\text{Ni} = 18.2$, $\text{Co} = 17.3$, and $\text{Zn} = 17.89$.

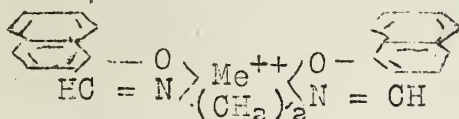
With the exception of zinc, the ionization involves the removal of an electron from a "d" orbital and the natural order expected in energy available to a reaction which replaces this electron would be $\text{Cu} > \text{Ni} > \text{Co}$ (3). Magnetic measurements in the case of Cu^{++} chelates are of no use since all possible types of bonding result in a single unpaired electron. In the case of Co^{++} and Ni^{++} , the magnetism of the solid chelates corresponds to three unpaired electrons for Co^{++} and two for Ni^{++} (6), indicating that they cannot be exclusively covalent planar dsp^2 compounds. (3). Calvin and Melchior (3) suggest that the structure of the

hybrid between covalent planar dsp^2 and ionic, involving one promoted electron in the 4 d shell in each case (3).

Calvin and Melchior also studied the stability of the O-formyl-naphthoxide chelates of the divalent zinc, copper, cobalt, and nickel ions. Since there are three such naphthol compounds, 3-formyl-2-naphthol, 2-formyl-1-naphthol, and 1-formyl-2-naphthol, they were able to verify the effect of "double-gondedness" on chelate stability (8), which had earlier been studied by Calvin and Wilson.

The same procedure was used in this case as in the others, which involved titrations of solutions of known acid, metallic ion, and organic anion concentration, with 0.1 M NaOH and determining the pH on a pH meter. The equilibrium here is the same as that originally mentioned for the chelates of salicylaldehyde. The experimental results in this case were only qualitative (7) since the very low solubility of the chelate prevented more accurate work. It was found, once again, that the cupric ion formed a more stable complex with the 1-formyl-naphthoxide ion than did either divalent cobalt or nickel ions (7).

The (2,4-diaza-1, 5-hexadiene)-dinaphthoxides, which have the structure,



appeared to form except in the case of zinc (7), in which case the metal ion appeared to react with two chelating anions. This apparent change is in agreement with the suggestion that the "d" orbital is involved since zinc, having no available "d" electron, would be expected to form a somewhat different type of compound.

It may be mentioned here that Calvin and Melchior (3) calculated the entropy of formation of bis-(5-salicylaldehydesulfonate)-copper, in an effort to establish the reasons for the stability of chelated compounds.

Recent Work:

At the March meeting of the American Chemical Society in San Francisco, Lawrence T. Quill and Joseph G. Stites, Jr., reported a study of the stability of copper and rare earth chelates of trifluoro- and hexafluoro-acetyl acetates (9) by the method mentioned above. This work is becoming increasingly important in ion-exchange methods for the separation of metal ions.

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May 10, 1949

Catalytic Decomposition of Aqueous Hydrogen Peroxide Solutions

I. Stability of Hydrogen Peroxide.¹

Hydrogen peroxide is thermodynamically unstable with respect to water and oxygen. In the absence of a catalyst, however, the rate of decomposition is exceedingly slow, especially in acids. Alkaline solutions decompose more readily, due to the formation of hydroperoxide ion OOH^- . The ionization constant is

$$K = [\text{H}^+] [\text{OOH}^-] = 2.4 \times 10^{-12}$$

so that

$$[\text{OOH}^-] = \frac{K [\text{OH}^-]}{K_w} = 240 [\text{OH}^-]$$

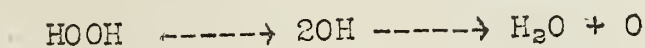
TABLE I

Stability of Aqueous H_2O_2 Solutions¹

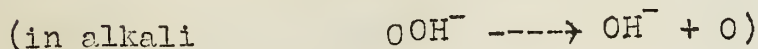
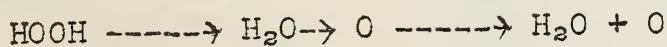
| % H_2O_2 | % NaOH | Rate of Decomposition |
|--------------------------|--------|----------------------------------|
| 6 | 0 | 2% per year |
| 90 | 0 | 1% per year at 30° C |
| | | 2% per day at 100° C |
| | | rapid at 140° C |
| 6 | 20 | 2% per day |
| | | 79% per day with commercial NaOH |

II. Decomposition of a Hydrogen Peroxide Molecule²

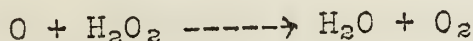
The hydrogen peroxide molecule probably decomposes by the breaking of an O-O bond: -----



or (assuming the existence of a tautomeric form)

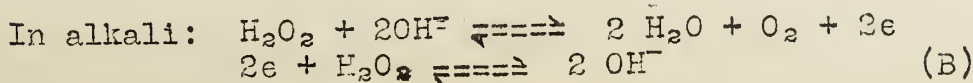
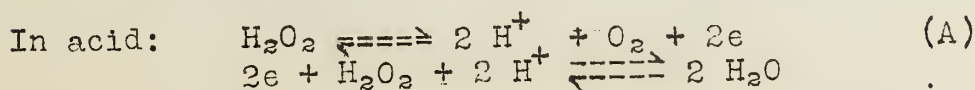


This may be followed by⁷



III. Auto-decomposition by Alternate Reduction-Oxidation

Hydrogen peroxide can act as either a reducing agent or an oxidizing agent: -----



Reactions (A) and (B) illustrate the mechanisms of the reactions. In each case the first (reducing) half-reaction must

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occur if the second (oxidizing) is to occur, and since the oxidizing reaction is difficult, it is reasonable that the decomposition occurs more readily in alkaline solution.

IV. Catalysis by Alternate Reduction-Oxidation

One of the principal ways in which catalytic decomposition of hydrogen peroxide may be effected is by alternate reduction and oxidation, so carried out that the reducing agent is reformed in the subsequent oxidation. For this to occur, it is necessary that (a) the reduced form of the catalyst be a poorer reducing agent than hydrogen peroxide, and (b) the oxidized form of the catalyst be a poorer oxidizing agent than hydrogen peroxide. Table II lists some of the substances of which the standard oxidation-reduction potentials are such that catalytic decomposition of hydrogen peroxide might occur (this should not be taken to indicate that it does occur in each case). It is based on Latimer's table.

TABLE II³

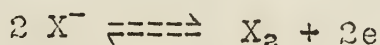
| Group | Acid or Base | Type of Solution | |
|-------|---|---|------------------|
| | | Acid | Base |
| 3B | | Ce(III) | |
| 5B | | V(IV) | |
| 6B | | Cr(III) | |
| 7B | Mn(IV) | Mn(II) | Mn(VI) |
| 8 | Ni(II) | Fe(II) | Co(II) |
| | Pd | Rh(III) | |
| | | Rh(IV) | |
| | Pt | Os | Ir |
| 1B | Ag | Au | Ag(I) |
| | | Au(I) | Ag(II) |
| 2B | Hg | Hg(I) | |
| 3A | Tl(I) | | |
| 4A | | Pb(II) | |
| 5A | N ₂ O, NO ₂ ⁻ | NO, N ₂ O ₄ | |
| | N ₂ H ₄ , NH ₃ | Bi(III) | |
| 6A | SeO ₃ ⁻² | S ₂ O ₃ ⁻² | Te |
| | | Sb | |
| | | Te(IV) | |
| 7A | ClO ₂ ⁻ , ClO ₃ ⁻ | Cl ₂ | OCl ⁻ |
| | Cl ⁻ , Br ⁻ | Br ₂ | OI ⁻ |
| | I ⁻ , IO ₃ ⁻ | I ₂ | |

The principal catalysts that operate by this method are the platinum metals¹⁷⁻²⁴ and the halide ions.¹⁴

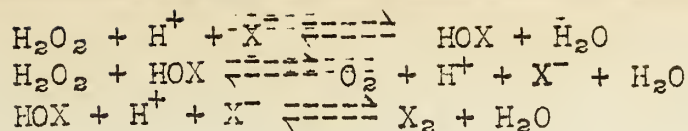
Examples of mechanisms:

(i) Bromine and Chlorine⁴

In acid solution, bromide and chloride ions catalyze the decomposition according to the half reaction

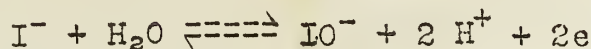


It is believed that the hypohalous acid is involved as intermediate, so that the mechanism is



(ii) Iodine⁴

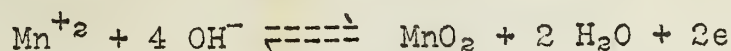
In acid solution, iodide ions catalyze the decomposition by similar mechanism, using the half reaction



Iodate ions also decompose hydrogen peroxide, probably by intermediate formation of iodosous acid.

(iii) Manganese⁵

Catalytic decomposition of hydrogen peroxide by manganese compounds involves the +2 and +4 states. The reaction does not occur in acid solution; nor does it occur in a neutral manganous solution. However, it is possible to decompose hydrogen peroxide catalytically by starting with neutral permanganate, due to the formation of manganese dioxide. The mechanism is probably due to the half reaction



V. Catalysis by Formation of Peroxy Compounds¹⁶

It is sometimes possible to prepare a peroxy compound from hydrogen peroxide that will subsequently lose oxygen to form the original oxy compound. Table III lists some reactions of hydrogen peroxide that form peroxyacids or their salts.

TABLE III⁶

| Oxy compound + H ₂ O ₂ -----> | Peroxy compound |
|--|---|
| M ₂ GeO ₃
(M = alkali metal) | M ₂ Ge ₂ O _{7.4} H ₂ O and
M ₂ GeO ₅ |
| stannic acid | H ₂ Sn ₂ O _{7.3} H ₂ O |
| G(IV) salts
(G = Ti, Zn, Hf, Ce) | H ₂ GO ₅
(more complicated with Th) |
| V ₂ O ₅ or vanadic acid | HVO ₄ or H ₃ VO ₅ |
| Cb(OH) ₅ ⁹ | HCbo ₄ |
| MGO ₃ ⁹
(G = Cb or Ta) | M ₃ GO ₈ |
| chromic acid | CrO ₅ |
| chromic acid in alkali | M ₆ Cr ₂ O ₁₆ |
| M ₂ CrO ₄ in acid | M ₂ Cr ₂ O _{13.2} H ₂ O |
| M ₂ GO ₄ ⁹
(G = Mo or W) | M ₂ GO ₈ |
| UO ₂ ⁺² | UO _{4.2} H ₂ O |
| MBO ₂ | MBO _{3.1/2} H ₂ O |
| Na ₂ B ₄ O ₇ | NaBO ₂ .H ₂ O _{2.3} H ₂ O |
| M ₂ CO ₃ | M ₂ CO ₃ .H ₂ O _{2.1/2} H ₂ O |
| HNO ₂ | HNO ₄ or O=NOOH |
| H ₂ SO ₄ | H ₂ S ₂ O ₈ and H ₂ SO ₅ |

The substances that form peroxyacids include⁶ (a) germanium and tin; (b) boron, carbon, nitrogen, phosphorous, sulfur, and possibly silicon and selenium⁸; and (c) transition elements of 4B, 5B, and 6B¹⁵; including Ce(IV), Th(IV), U(VI); and possibly Fe(III)⁷. Cases of catalytic decomposition have been reported only for case (c) above. These include (i) alkali chromates and dichromates in dilute acid¹⁰; (ii) mixtures of sodium molybdate and sodium tungstate in the presence of ferric sulfate in very dilute sulfuric acid¹¹; and

(111) vanadium pentoxide in cell 12, 13

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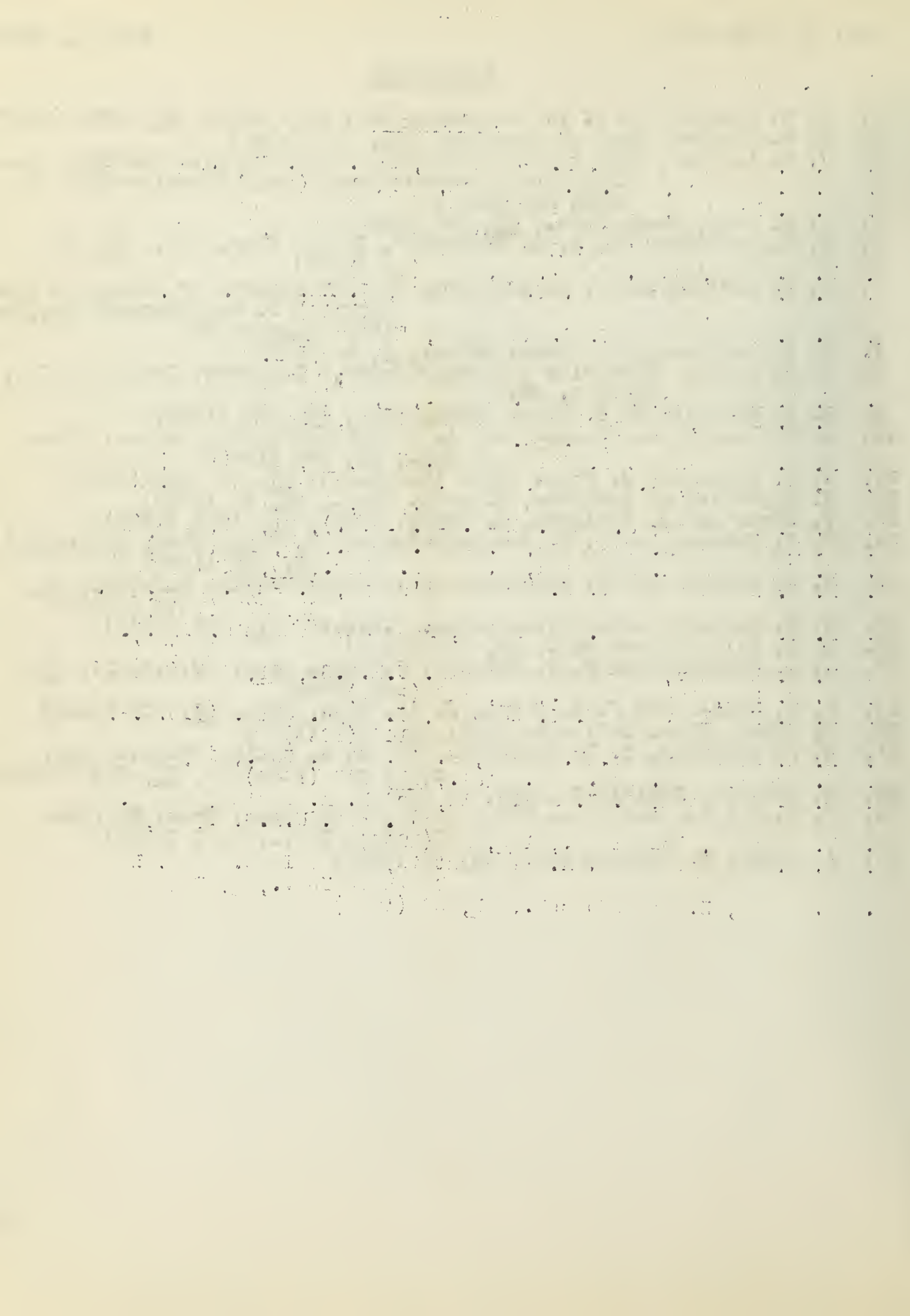
(111) vanadium pentoxide in cell 12, 13

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ACIDIC AND BASIC PROPERTIES OF OXIDES

A. E. Taylor

May 10, 1949

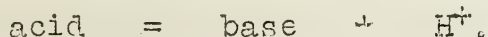
I. Introduction

The Lux theory of acid-base relations in oxide systems (8), later modified by Flood (3,4,5), could have gained considerable attention were it not for the existence of the more general Lewis concept. The modern trend is towards generalization of acid-base reactions. The Lewis concept permits the correlation of many different reaction types and thus improves our understanding of these phenomena. From this view point, the Flood theory opposes the modern trend.

II. Some Concepts of Acids and Bases (1,7).

1. The Arrhenius Theory, with Debye-Huckel modifications for strong electrolytes.
2. The Bronsted -Lowry Concept.

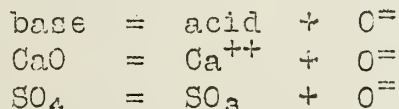
Acids are defined as substances capable of splitting off the proton; bases as substances capable of combining with protons.



However free protons do not exist in any solvent. Thus the above dissociation depends not only upon the intrinsic acid character of the solute but also upon the basic character of the solvent. This theory cannot be extended to none-protonic systems.

3. The Lux - Flood Concept.

This theory was developed to compensate in part for the limitations of the Bronsted theory. The two are analogous.



This concept is limited to oxide systems. It is not readily extended to similar phenomena which can occur in fused sulfides. Still this concept is more desirable than the "acid analogue" approach offered by proponents of the Bronsted theory.

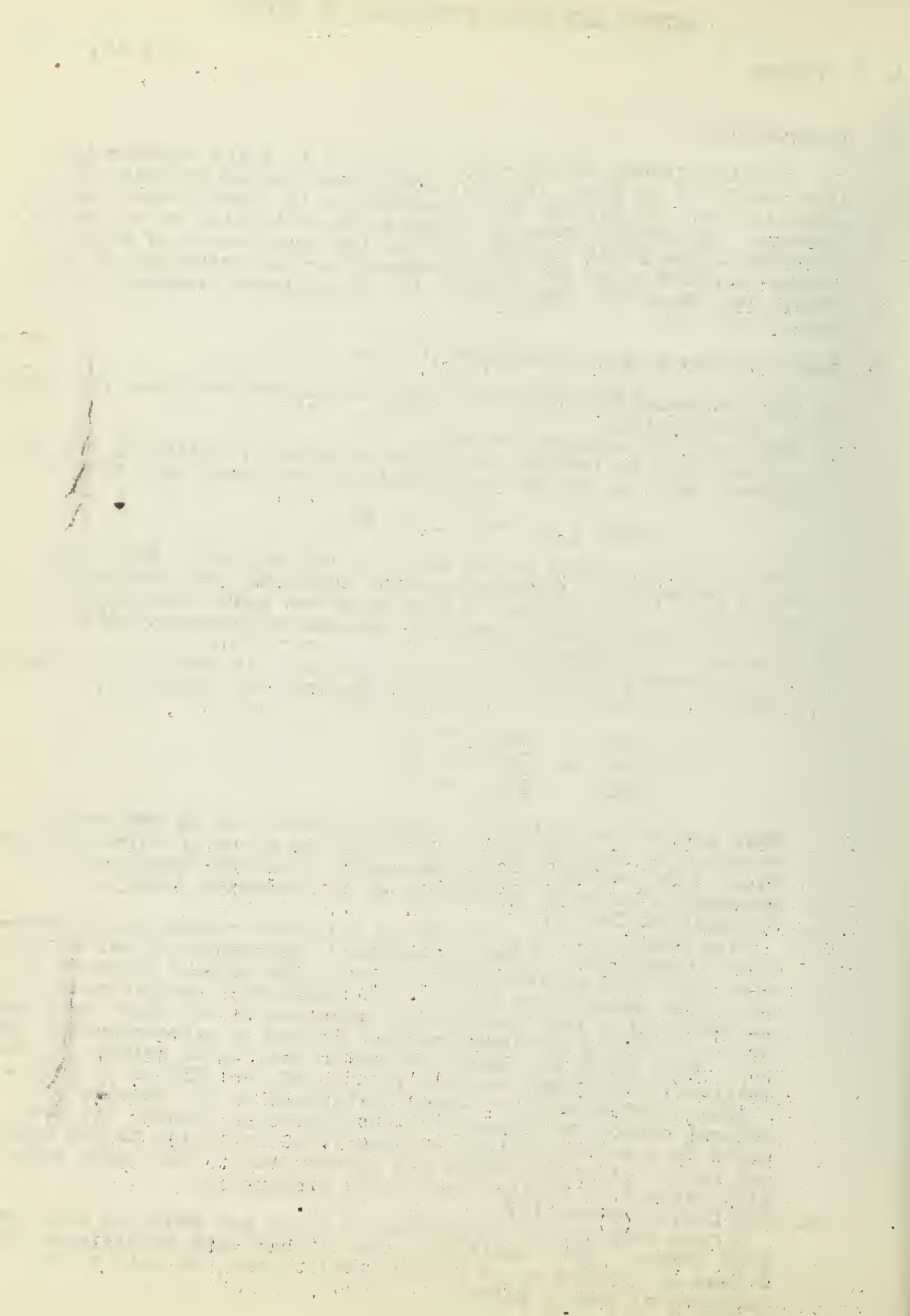
4. The Solvent Theory.

This theory is one which limits acid-base phenomena to behavior in solution. "Neutralization is the union of solvo-positive ions with solvo-negative ions". "An acidic solution is one which contains as one of the predominant species present a solvo-positive ion, and a basic solution is one which contains as one of the predominant species present a solvo-negative ion" (1). Thus NH_4Cl and KNH_2 form acidic and basic solutions, respectively, in liquid ammonia just as HCl and KOH do in water.

Consideration of "acid-base" relations in the absence of a solvent cannot be attempted by this theory. Ginell (1) proposes that such reactions be classified according to the types and number of bonds broken and formed; but is extremely vague with respect to application to his proposals.

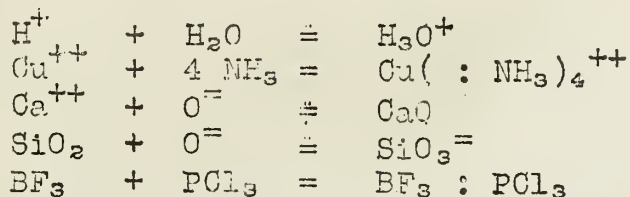
5. The Lewis Concept (1)

A more fundamental definition of acids and bases is used in this theory. The result has been a break with traditional ideas. A base is defined as an electron pair donor, an acid as an acceptor of such a pair.



The reaction product, or neutralization product, therefore contains a coordinate or dative bond between the acid and the base.

acid + base = neutralization product



It is evident that this concept includes not only "acids" and "bases" but also substances which have not hitherto been recognized as such. Also substances formerly regarded as acids or bases do not necessarily retain this connotation. Phillips (10) has raised a fundamental objection to the theory. From studies of bond distances, it appears that the coordinate or dative bond is not as common as proponents of the Lewis theory suggest.

From the Lewis viewpoint, it may be concluded that acid-base behavior is due to differences in electron structure.

6. The Usanovich Concept (1).

The Lewis concept is extended here to include redox reactions. Both acids and oxidizing agents are electron acceptors, the former sharing an electron pair and the latter incorporating completely the electrons involved. The difference appears to be in degree and not in type.

III. Properties of Acidic and Basic Oxides.

Properties suitable for investigation of the nature of fused melts are limited. Information obtained from density, viscosity, refractive index, and X-ray diffraction data serve only for the determination of average composition. Depression of the freezing point and electrical conductivity may be related to structure. Unfortunately, unknown factors affect the data so greatly that interpretation is not possible (8). Flood (3) has suggested the partition of solutes between phases as a possible approach. Other experimental methods have been investigated:

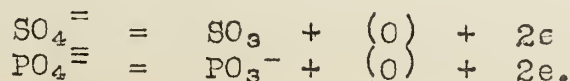
1. Potentiometric measurements (2,8).
2. The use of indicators (5,9).
3. Composition as a function of equilibrium pressure (3,4,5,6).

The Flood concept was developed from consideration of the phenomena observed in these experiments.

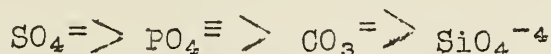
1. Potentiometric measurements.

(a) Oxygen overpotential in molten salts (2).

Potentials were determined in pure Li-Na sulfate melts and in Li-Na fluoride melts containing sulfate, phosphate, carbonate and silicate. The observed effects agreed with the assumption that the oxygen potential is determined by reactions of the type



The overpotential within a given range of temperature and current density was found to decrease in the order



i.e. in the order of decreasing strength of the X-O bond or in the order of increasing basicity.

(b) Potentiometric determination of the oxygen ion concentration (8).

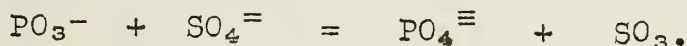
The Lux theory was introduced in a paper describing the behavior of the potential of a gold electrode as a function of the oxygen ion activity in fused Na-K sulfate. Rhodium served as a reference electrode. The effects of Na_2O , Na_2CO and NaPO_3 were studied. The oxygen ion activity was assumed equal to the concentration of Na_2O and the symbol pO was given the same significance that the symbol pH has in water.

$$pO = -\log n \text{ where } n = \frac{\text{moles Na}_2\text{O}}{\text{moles Na}_2\text{SO}_4, \text{K}_2\text{SO}_4, \text{Na}_2\text{O}}$$

Small amounts of Na_2CO_3 were decomposed completely in the melt. Larger quantities decomposed incompletely and the ratio of carbonate to oxide or $\frac{(\text{CO}_3^{\equiv})}{(\text{O}^{\equiv})}$ could be determined

from the partial pressure of CO_2 over the melt.

An acidic melt was produced by the addition of NaPO_3 to the system. The gold electrode immediately assumed a positive charge relative to the reference electrode. The potential difference gradually decreased as the following reaction took place:



When PO_3^- and PO_4^{\equiv} were added to the melt in the mole ratio 1:1 this reaction became so slow that the melt was effectively buffered. The value for the equilibrium constant,

$$K = \frac{(\text{PO}_3^-)(\text{O}^{\equiv})}{(\text{PO}_4^{\equiv})} = 5 \times 10^{-6}$$

was calculated from the data.

2. The use of indicators (3,9).

The effects of various oxides on B_2O_3 melts were studied by means of the Cr III / Cr VI indicator (9). Alkaline melts are yellow, acidic melts are green. The following oxides were investigated: Li_2O , Na_2O , K_2O , BeO , MgO , BaO , PbO , Al_2O_3 , La_2O_3 ; and SiO_2 , P_2O_5 . The observations were plotted on composition diagrams and revealed a number of peculiarities.

Comparison of Li_2O , Na_2O , and K_2O showed the expected increase in basicity with increasing atomic number. However, for Li_2O , the variation of the neutral point of the melt was peculiar. Over a range of Li_2O concentration this point was located in the region assigned to acidic oxides.

The replacement of Na_2O by bivalent di- or tri-valent oxides produced startling results. When small amounts of these oxides are present, the neutral point of the melt lies in the region

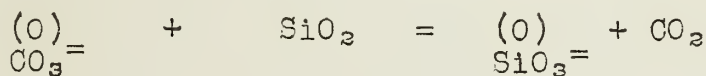
assigned to strongly acidic oxides. As the composition of the melt approaches that of the metaborates (BO_2^-), the neutral point approaches the region assigned to oxides which are less acidic than B_2O_3 .

SiO_2 was found to behave like a slightly weaker acid than B_2O_3 . P_2O_5 behaved like a strong acid.

The explanation of the phenomena observed on addition of basic oxides to B_2O_3 must lie in the behavior of B_2O_3 . The explanation offered by Flood (3,4,5) appears more satisfactory than that given by Lux (9). According to Lux, variations in the effect of the basic oxides were found to be due to differences in the degree of dissociation of these oxides which in turn depends upon the ionic character of the metal-oxygen bonds. Hence this procedure may be used for the determination of the degree of dissociation of oxides in fused melts. BaO , PbO , and La_2O_3 were found to produce the greatest "acidifying" effect on B_2O_3 melts; MgO a somewhat smaller effect; and BeO and Al_2O_3 still smaller effects.

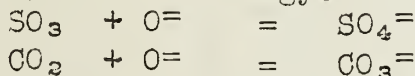
IV. The Flood Concept (3,4,5).

The characteristic process of acid-base reaction in oxide system is the transfer of an oxygen ion from one state of polarization to another.



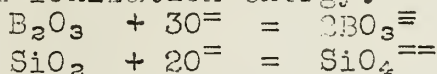
Acid-base reactions may be classified according to the ionization energy of the central atom.

1. Atoms with high ionization energy.



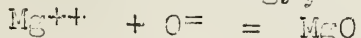
The acid-base transition is accompanied by an alteration of the coordination number of the central atom for oxygen.

2. Atoms with medium ionization energy.



The acid-base transition is associated with macromolecular structure. The conversion of the acid to the base is a process of breaking oxygen bridges in the polymer.

3. Atoms with low ionization energy, i.e. typical cation forming atoms.

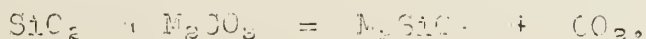


The acid-base transition is associated with the formation of an oxide phase.

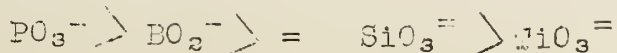
Relative acidity may be determined from the following equilibria under constant CO_2 pressure.



The further the reaction proceeds to the right, the stronger is the acid, M^{++} , and the weaker is the base, MO . Similarly the acidity of the acidic oxides (SiO_2 , B_2O_3 , etc.) may be evaluated relative to CO_2 .



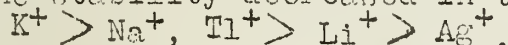
Studies on the latter systems yielded the following order of acid strength:



The polarizing effect of the cation.

It was observed that the strength of the polyacids was largely dependant upon the cation present. For example, the behavior of B_2O_3 in melts of Li, Na, and K carbonate can be considered. The amounts of CO_2 expelled from the melts corresponded to the formation of the following anions: in Li_2CO_3 , BO_3^{2-} ; in Na_2CO_3 , BO_2^{2-} ; and in K_2CO_3 , BO_2^- . The stability of the oxygen bridge in the polyacids must be assumed to decrease in the presence of the alkali ions in the order $K^+ > Na^+ > Li^+$. This behavior was noted by Lux (9). In silicate systems the cation effect was more pronounced, in titanate systems it was not as great. The viscosity of acid silicate melts was also observed to decrease in the same order.

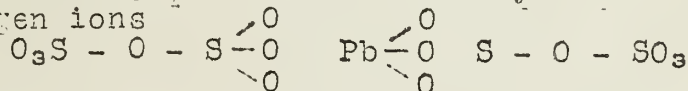
A related phenomenon is the thermal instability of the pyrosulfates (4). The stability decreased in the following order:



Therefore this phenomenon cannot be explained upon the basis of size alone. It is known that the polarizing effect of an ion having 18 electrons in its outer shell is greater than that of an ion possessing a rare gas configuration, provided that the ions are comparable in size.

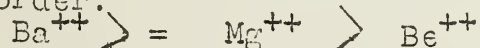
Further evidence of the polarizing effect of the cation was obtained from various other studies.

The addition of sodium, lithium and lead sulfate to potassium pyrosulfate (4) showed that, at 662° , Li^+ effected the expulsion of $1/2$ mole SO_3 per mole Li^+ and that Pb^{++} effected the expulsion of 2 moles SO_3 per mole. Lead may be considered to coordinate six oxygen ions



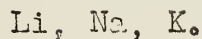
The groups are thereby polarized to the extent that the S - O - S bridge cannot be maintained. At $775-780^\circ$ the lithium ion effected the expulsion of about 1 mole SO_3 per mole, thus showing that the coordination effect of this ion is a statistical phenomenon.

Similar behavior was observed in borate melts (9). The number of B - O - B bridges broken by the cation was found to decrease in the order:



The importance of cation size becomes evident, provided that the polarizing effect exceeds a certain amount. Ba^{++} is large enough to coordinate 12 oxygen ions; Mg^{++} , 6; and Be^{++} , 4. Theoretically these ions are capable of breaking the corresponding number of oxygen bridges.

A semi-quantitative treatment of the relative acidity of the polyacids, analogous to Bjerrum's method for complex formation, was developed (5). The values for the equilibrium constants were found to decrease with decreasing polarizing effect of the cation i.e. in the order



A. E. Taylor

May 10, 1949

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THESIS REPORT

FLUORINATION OF INORGANIC HALIDES

P. J. Pizzolato

May 17, 1949

Since other sulfur oxyhalides had been successfully fluorinated in a stepwise manner (SO_2Cl_2 , SOCl_2), it was of interest to study the fluorination of the less familiar pyrosulfuryl chloride, $\text{S}_2\text{O}_5\text{Cl}_2$. It was the purpose of this investigation, therefore, to determine the conditions under which this compound could be fluorinated and to determine the properties, both chemical and physical, of the two fluorine derivatives, the chlorofluoride, $\text{S}_2\text{O}_5\text{ClF}$, and the difluoride, $\text{S}_2\text{O}_5\text{F}_2$.

Inasmuch as the Swarts method had been successfully applied to the fluorination of both thionyl and sulfuryl chlorides (1,2), it appeared to be the most promising method and was the first tested in this study. Since preliminary study indicated that little or no reaction took place when antimony trifluoride was used as fluorinating agent in the absence of a catalyst, antimony pentachloride catalyst was used in all experiments involving the Swarts method.

Previous experience with this type of reaction indicated that the production of partially fluorinated products, i.e., chlorofluorides, is favored by what is known as the "forcing" technique, which consists in bleeding off the gaseous products from the generator flask and collecting them just as rapidly as they are formed (3,4,5). Accordingly, the first run was carried out at as low a pressure as possible, the gaseous products being bled off continuously through a slightly cracked stopcock and collected as rapidly as possible, at the risk, of course, of some of the starting material being carried over.

The reaction was carried out in the usual Swarts type generator consisting of a modified 1-liter Claisen flask with delivery sidearm connected to a dropping funnel for catalyst and with the main neck fitted with a screw feed-containing side arm for slow addition of the fluorinating agent, antimony trifluoride. The 1-rpm stirrer with which the generator was equipped served mainly to prevent the cake of solid which forms in the reaction from adhering to the flask bottom. Both moving parts, the stirrer and screw-feed shafts were sealed through gas-tight packing glands.

When it was observed that the reaction was slow at room temperature, the reaction mixture was heated to about 50° to accelerate the reaction. Fractionation of the reaction products indicated that considerable decomposition had taken place and this was at first believed to be due to the heating required. Neither of the desired fluorine derivatives was obtained, the main product of the reaction being sulfuryl chlorofluoride, SO_2ClF , in about 35% yield, formed presumably by the fluorination of the decomposition product SO_2Cl_2 , although according to earlier work this latter compound is fluorinated by the Swarts method only when the reaction is carried out under pressure (2). Other products isolated in the fractionation were small amounts of SO_2Cl_2 (about 7%), SO_2 , Cl_2 , together with some of the starting material.

As mentioned above sulfuryl chloride was successfully fluorinated by the Swarts method only under high pressures

(90-100 p. s. i.), these conditions producing good yields of the chlorofluoride but, surprisingly, none of the difluoride. It thus appeared that pressure might possibly be the determining factor in this case also, and the next two experiments were carried out under pressure, the first at about 40 p. s. i., the second at about 90.

It was, perhaps, unfortunate that to obtain these pressures it was necessary to heat the reaction mixtures considerably, to a temperature in excess of 150°, for example, in the latter case. This may account possibly for the decomposition which resulted in these experiments. Fractionation of the reaction products yielded again as the main product, sulfonyl chlorofluoride (about 45% and 30% yields in two runs) and smaller amounts of the other decomposition products encountered earlier.

It seemed likely at this point that excessive temperatures was the troublesome factor. Therefore, to achieve pressures in excess of one atmosphere, without the need for heating the reaction mixture, anhydrous hydrogen fluoride (v. p. of about 1½ atm. at room temp.) was used as the fluorinating agent. The reaction was carried out in an iron vessel and an iron column attached to the reactor was used for the attempted preliminary rough separation of the excess HF from the reaction products. Separation of the excess HF from the reaction products proved to be such a great problem that this method was subsequently abandoned.

In an attempt to determine whether the desired fluorine derivatives were stable under ordinary conditions an effort was made to obtain them by another and unrelated method: the chlorofluoride by the dehydration of an equimolar mixture of fluosulfonic and chlorosulfonic acids by means of phosphorus pentoxide; and the difluoride by the dehydration of fluosulfonic acid. Since the starting material, $\text{S}_2\text{O}_5\text{Cl}_2$, can be easily prepared by the dehydration of chlorosulfonic acid, it was reasonable to expect at least the corresponding reaction with fluosulfonic acid to be possible. Then, too, if the difluoride could be obtained in this way, a possible new route to the chlorofluoride would present itself, i.e., chlorination of the difluoride. The results of these experiments, however, were inconclusive. While these compounds may well have been formed in the dehydration reaction mixtures, all attempts to isolate them by distillation, even at low pressures, were without success.

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Electrochemical Studies of Some Coordination Compounds

Bodie E. Douglas

May 17, 1949

It has been well established that the shift in the reduction potential of a complex ion compared to the aquated ion is a quantitative measure of the extent of stabilization by coordination (1). This is expressed as the dissociation constant for the complex. The number of groups attached to the metal ion can also be determined from the reduction potentials if enough data are available. However, these calculations are valid only if the electrode processes involved are reversible. The polarograph is a convenient instrument for obtaining the necessary data over a wide range of potentials.

This project was begun as a study of the electrochemistry of some coordination compounds of manganese. The first system studied was the Mn(III)-Mn(II) couple in the presence of an excess of pyrophosphate. The Mn(II) was oxidized to Mn(III) with KMnO_4 and the oxidation followed potentiometrically. It was found that the potential varied with the pH and that the rate of change of potential with pH also varied continuously. This system was abandoned when it was learned that a similar study was soon to be published (2).

Unsuccessful studies of the Mn(III)-Mn(II) couple were attempted in the presence of orthophosphate and fluoride. The former gave insoluble phosphates over a wide pH range. The fluoride system was complicated by the difficulty of measuring the pH of a highly colored solution containing fluoride ion and a strong oxidizing agent. Polarographic studies of the Mn(III)-Mn(II) system in the presence of sodium tartrate proved futile, since the electrode process was found to be irreversible.

The reductions of Mn(III) to Mn(II) and Mn(II) to Mn(I) were studied polarographically in the presence of KCN. The first reduction step occurs at a potential too positive for an analysis of the wave. The reduction of Mn(II) to Mn(I) was found to be reversible, $E_1 = -1.31$ volts vs. S.C.E. Because no data are available for the reduction of the aquated Mn(II) ion to Mn(I), the ratio of the dissociation constants could not be determined. All three ions show a coordination number of six.

Since it was apparent that few reversible systems would be found for manganese complexes, studies of complexes of chromium were undertaken. The ammoniac, ethylenediamine, diethylenetriamine, o-phenanthroline and dipyridyl complexes were studied polarographically and all were found to be irreversible. Interesting adsorption effects at the electrode surface were noted in the case of o-phenanthroline and dipyridyl and these were investigated by determining the electrocapillary curves in the presence of these complexing agents.

Chromium(III) was found to reduce irreversibly in the presence of sodium tartrate and tartaric acid. No reduction wave was observed before the discharge of the indifferent electrolyte for either potassium trioxalatochromate(III) or tris(glycine)chromium(III).

Potassium hexathiocyanatochromate(III) was found to reduce reversibly to the corresponding hexathiocyanatochromate(II) complex. $E_1 = -0.80$, $K_{ox}/K_{red} = 2.3 \times 10^2$.

By this time it was obvious that manganese and chromium were not very desirable elements for this type of study. Cadmium was chosen as the next element to be investigated. Cadmium was found to reduce reversibly to the amalgam in the presence of ethylenediamine, propylenediamine and diethylenetriamine. The formulas, half-wave potentials, (in 1 M complexing agent) and dissociation constants are respectively: Cd(en)_3^{++} , -0.93 , 1.7×10^{-12} ;

$\text{Cd}(\text{pn})_3^{++}$, -0.94, 1×10^{-12} ; $\text{Cd}(\text{dien})_2^{++}$, -0.99, 1.7×10^{-14} .
Investigations are now in progress of the reductions of $\text{Cd}(\text{II})$ in the presence of triethylenetetramine, thiocyanate, pyridine, o-phenanthroline and dipyridyl.

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Stereochemistry of Inorganic Complex Compounds

Leo F. Heneghan

May 17, 1949

Resolution of Racemic Tyrosine. During recent years it has been reasonably well established that inorganic complex compounds which have coordinated optically active groups of the same configuration are more stable than those composed of groups of different configurations around the asymmetric central atoms. This leads to the idea of using this phenomenon to separate optically active isomers by means of inorganic complexes. Although no exceptions to the above postulate have been observed, we cannot overlook the possibility that the differences in stability of the above two types of compounds may be very slight.

This study is an attempt to resolve the amino acid tyrosine by means of complexes of cobalt. The problem was approached from two points of view. In the first set of reactions $[\text{Co } \underline{\text{L}}\text{-pn}_2\text{Cl}_2]$, Cl was allowed to react with a 100% excess of racemic tyrosine. If the stabilities of $[\text{Co } \underline{\text{L}}\text{-pn}_2\text{L-tyro}]\text{Cl}_2$ and $[\text{Co } \underline{\text{L}}\text{-pn}_2\text{D-tyro}]\text{Cl}_2$ are sufficiently different, then in the presence of excess racemic tyrosine, the less stable complex might give way to the more stable one. This would give at least a partial resolution of the acid.

The second set of reactions were carried out between $[\text{Co } \underline{\text{L}}\text{-pn}_2\text{rac-tyro}]\text{Cl}_2$ and levo-propylenediamine in the ratio of 2:1. If one isomer of tyrosine is more readily replaced by the active amine than the other, then this too might give a partial resolution of tyrosine.

Although the work has not been completed, it appears that under the conditions used the complexes of tyrosine may not show sufficiently different stabilities to make resolution possible.

Diastereoisomers of $[\text{Pt } \text{en}_2\text{d-tart}]\text{ (NO}_3)_2$

Johnson (1) showed that the usual preparation of $[\text{Co } \text{en}_2\text{d-tart}]\text{Cl}$ resulted in the formation of a mixture of the two diastereoisomers. Further, the relative amounts of the two isomers may be changed by variations in the experimental conditions.

This investigation was undertaken to determine whether the corresponding platinum complexes would behave in a similar manner.

During the preparation of the starting material $[\text{Pt } \text{en}_2\text{CO}_3]\text{ (NO}_3)_2$ from trans $[\text{Pt } \text{en}_2\text{Cl}_2]\text{Cl}_2$ according to the method given by Basolo (2), it was found that the coordinated chloro groups were not as readily replaced as was reported.

In view of these results it seemed necessary to find a new method for the preparation of cis $[\text{Pt } \text{en}_2\text{CO}_3]\text{ (NO}_3)_2$. This compound would provide a means of preparing many corresponding cis compounds of platinum.

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Polarography in Liquid Ammonia

Carlyle E. Shoemaker

May 17, 1949

Continuing the work of Laitinen and Nyman (4,5) the reduction processes of other ions in liquid ammonia were studied.

When a mercury pool anode was used as a reference electrode in a single compartment cell containing the reducible ion, the anodic oxidation product of mercury was shown to be the mercuric ion.

Thallous ion showed a reversible reduction to the amalgam. The observed values of the diffusion currents of thallous ion were found to be in essential agreement with those calculated from the conductance data of Franklin and Kraus (3).

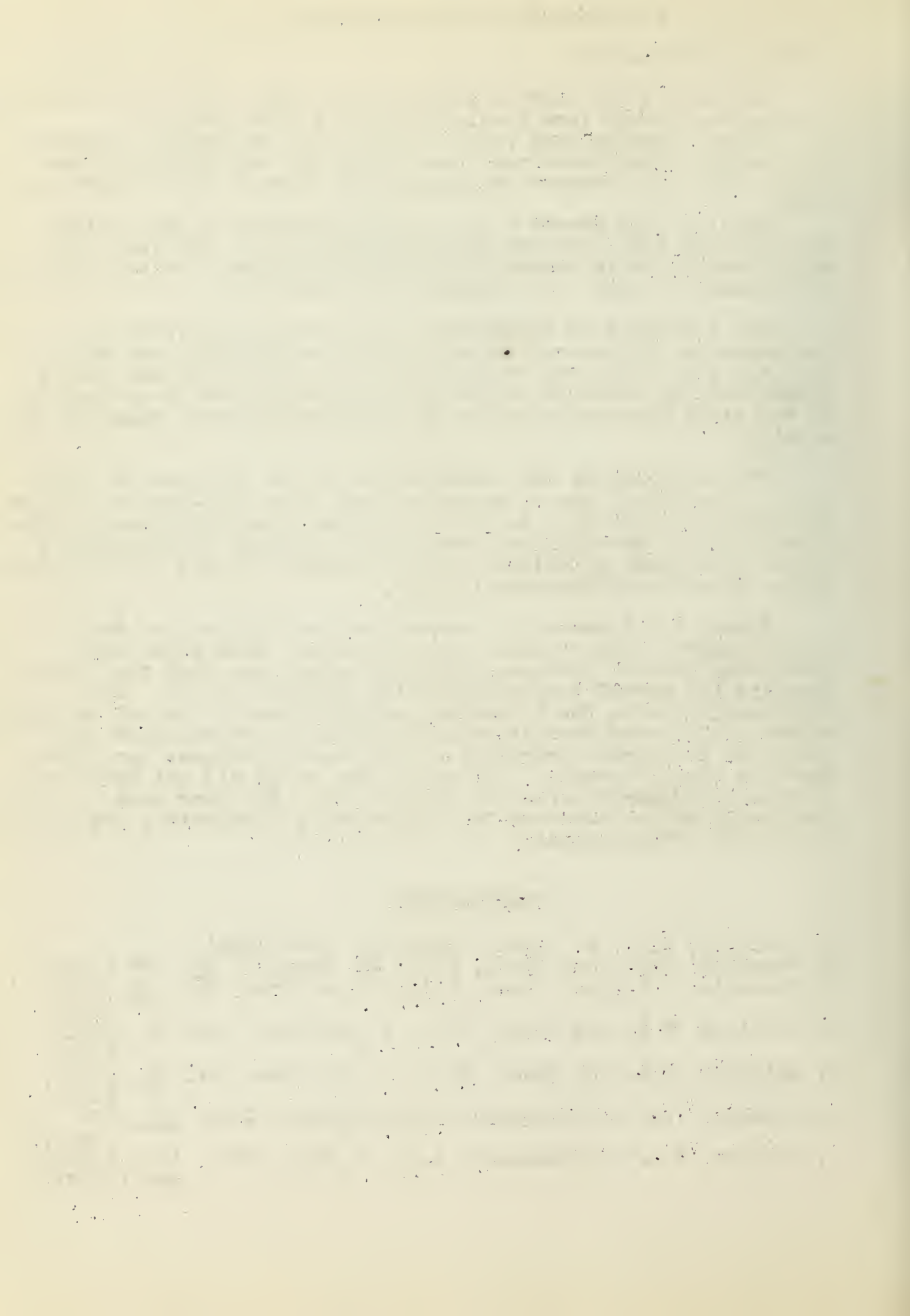
The reduction of oxygen in liquid ammonia was found to be analogous to the process in water solution with the exceptions that the slopes of both waves approached more nearly the values calculated for reversible reduction processes, and the potential of the first wave was found to be dependent to some extent on the acidity.

The reduction of the ammonium ion to the amalgam was found to be a reversible one electron process. The half-wave reduction potential was very near to that of sodium. As in the case of the alkali metals, the diffusion currents were found to be somewhat higher than those calculated from the conductance data of Franklin, Kraus, Pleskov and Monosson (2,3,6).

Copper was found to be reduced in two steps as are the copper ammonia complexes in water solution. Both steps were reversible and the diffusion currents calculated from the data of Franklin (1) agreed very closely with observed values. The difference between the half-wave potential and the normal potential of the ammine complexes in water solution at 25° was used to calculate the normal potential of the copper, cuprous ion electrode in liquid ammonia. The calculated value did not agree with previously measured values of Pleskov (7). The fact that a correction could not be made for the difference in temperature may partly explain the disagreement.

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J. C. Brantley

OBSERVATIONS ON THE RARE EARTHS: SOME STUDIES IN THE ABSORPTION SPECTRA

Introduction: In spite of intensive work on the absorption spectra of the rare earth elements, it is still impossible to assign definitely any given transition in the energy levels to any given band in the spectra. It is now generally accepted that the transitions arise in the 4f level of the atom between energy levels of differing L and S quantum numbers, but with the individual l values remaining the same. Although such transitions are forbidden by quantum rules, it is assumed that they are allowed by the presence of a potential field, a resultant of the deformation of the ion and an interaction of the 4f level with the potential field due to the neighboring negative ions.

The present study was undertaken to investigate the spectrophotometric estimation of the rare earth ions in solutions of their salts and to measure changes observed in the spectra when complexing anions are present with the idea of possibly establishing the compositions of any complex ions by the use of the method of continuous variations and the method of limiting logarithms.

Results: The complete absorption spectra from 2200 Å to 10000 Å were determined for many of the rare earth ions in chloride, nitrate, acetate, and perchlorate solutions. An analytical procedure was established by determining that the absorption coefficients of all the rare earths studied, except gadolinium adhered to Beer's Law of light absorption.

A spectrophotometric study of the effects on the neodymium spectrum of the acetate, tartrate, and ethylenediamine tetracetate ions was carried out. Only two complex ions were rather definitely established to be present in solutions of neodymium chloride with any of these ions. Using the method of continuous variations it was found that ethylenediamine tetracetate ion apparently forms 1:1 and 2:1 complexes with neodymium.

Evidence was found that the neodymium ion forms a stable ionic configuration in solutions with the acetate ion or tartrate ion when either of these ions is present in a ratio to neodymium of 6:1. The tartrate-neodymium arrangement is stable only in basic solution. At the 6:1 ratio of tartrate to neodymium, the 5750 Å band of neodymium chloride was split into three bands at 5765 Å, 5805 Å, and 5855 Å. All the bands were shifted to the red.

The ethylenediamine tetracetate ion, when added to neodymium chloride solutions, caused a splitting of all the bands on the red side of 5100 Å. The splitting was found to be in direct proportion to the concentration of this ions, the 5750 Å band being split into six well-defined bands between 5750 Å and 5860 Å for the largest concentration of ethylenediamine tetracetate. The splitting of the bands by the tartrate and ethylenediamine tetracetate is ascribed to an internal Stark effect.

The chloride ion apparently forms stable configurations with the erbium ion in perchlorate solutions when the ratio of chloride to erbium is 3:1 or 6:1. The bands of erbium are found to be split into component levels when ethylenediamine tetracetate ion is added to erbium perchlorate solution.

Theodore H. Dexter

May 24, 1949

STRUCTURE OF AZO LAKES

As the result of numerous studies by Morgan, his co-workers, and others, the so-called "lakes" used in the dye industry have proved to be coordination compounds of the inner complex type. The present work was undertaken to explore the formation, structure, and properties of lakes prepared from azo dyes and salts of tetravalent metals. A secondary problem, the nature of the coordination bond between the azo group and the central metal ion was investigated as an outgrowth of the original exploratory studies.

It was found that the combination of covalent metallic chlorides with azo dyes in non-aqueous solvents such as ether and glacial acetic acid produces addition compounds but not inner complexes. The ratio of dye molecules to metal atoms in these addition compounds seldom can be expressed in small whole numbers. Such formulas as $H_2PtCl_6 \cdot xH_2C_6O_4 \cdot y$ are evident from empirical elementary analyses. These compounds (or aggregates) are hydrolyzed readily by water to yield the original dye and the metal chloride, and are therefore of doubtful promise to the dye industry.

The fundamental problem of the nature of the coordination bond between the azo group and the central metal atom was studied by the attempted preparation of lakes from o-azophenol, salicyl-o-aminophenol and o,o'-dihydroxystilbene. To produce the high-melting form of the latter organic compound a new synthesis was developed which consisted of the pyrolysis of o,o'-dimethoxybenzalazine in diphenyl ether and the subsequent cleavage of the ether groups with potassium hydroxide in ethylene glycol.

Previous studies and the present work show that both o-azophenol and salicyl-o-aminophenol form stable inner complexes with metal salts. However, recent experiments indicate that this property does not extend to the high-melting (trans) form of dihydroxystilbene. Thus the presence of nitrogen atoms in the azo group appears to be important to the formation of stable inner complexes.

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Observations on the 8-Hydroxyquinoline and Related Derivatives
of Gallium, Indium and Thallium

Gallium forms a well characterized oxinate, the composition of which closely approximates that given by the formula, $\text{Ga}(\text{C}_9\text{H}_6\text{NO})_3$ (2). This compound begins to precipitate from solution at an average pH of 2.82 (75°C.) and the precipitation appears to be complete at a pH of 3.10. Gallium oxinate has been proposed for the gravimetric determination of small amounts of gallium (2). The oxine chelated to the gallium may be determined by bromate titration and the gallium content of the compound calculated from this.

The absorption spectra of solutions of gallium in chloroform were investigated by means of an unmodified Beckman Model DU Quartz Spectrophotometer (used throughout this work). All solutions observed were placed in 5.0 cm. demountable absorption cells with quartz windows. In the wave length range 252-600 m μ , four absorption peaks were observed at 254-268, 320, 335 and 392.5 m μ . The last three peaks were found to obey Beer's Law, and the 392.5 m μ peak was found suitable for use in colorimetric procedures within the concentration range 0.1-2.5 mg. of gallium (as the metal) per liter of chloroform.

The extraction of gallium from aqueous solutions was investigated using oxine in chloroform as the extracting agent. The extraction of the metal was found to be complete in the pH region, 3.0-6.2 under the conditions outlined. This extraction procedure makes possible a direct colorimetric estimation of the gallium present in an aqueous solution by extraction and spectrophotometric examination of the extract at 392.5 m μ .

Gallium dibromoxinate (5,7-dibromo-8-hydroxyquinolate), $\text{Ga}(\text{C}_9\text{H}_4\text{Br}_2\text{NO})_3$, was prepared and chloroform solutions were examined spectrophotometrically in the region 249-800 m μ . Four absorption peaks were observed at 268.5, 331, 344 and 410 m μ . The 410 m μ peak was found to obey Beer's Law and be suitable for the determination of traces of gallium in aluminum ores. The lower and upper limits of the colorimetric determination was found to be 0.062 and 1.00 mg. of gallium (as the metal) per liter of chloroform, respectively.

Gallium dichloroxinate (5,7-dichloro-8-hydroxyquinolate), was prepared (1), for the first time, in a manner similar to that used for the preparation of the corresponding dibromoxinate. The formula was found to be $\text{Ga}(\text{C}_9\text{H}_4\text{Cl}_2\text{NO})_3$, and the precipitation was quantitative. The absorption spectrum in chloroform solution was found to be similar to that of the corresponding dibromoxinate.

Chloroform solutions of aluminum oxinate and dibromoxinate were examined spectrophotometrically and the absorption spectra were found to be closely similar to those of the corresponding gallium compounds.

A solution of indium oxinate, $\text{In}(\text{C}_9\text{H}_6\text{NO})_3$, was examined by means of the spectrophotometer in the wave length region 295-500 m μ . Characteristic absorption peaks were observed at 320, 336 and 395 m μ .

Chloroform solutions of thallium (I) oxinate, $\text{Tl}(\text{C}_9\text{H}_6\text{NO})_3$, prepared by the method of Rey (3), were examined spectrophotometrically in the region 300-1000 m μ . Although the solutions of this compound were found to be both thermally and photochemically active, the absorption spectra

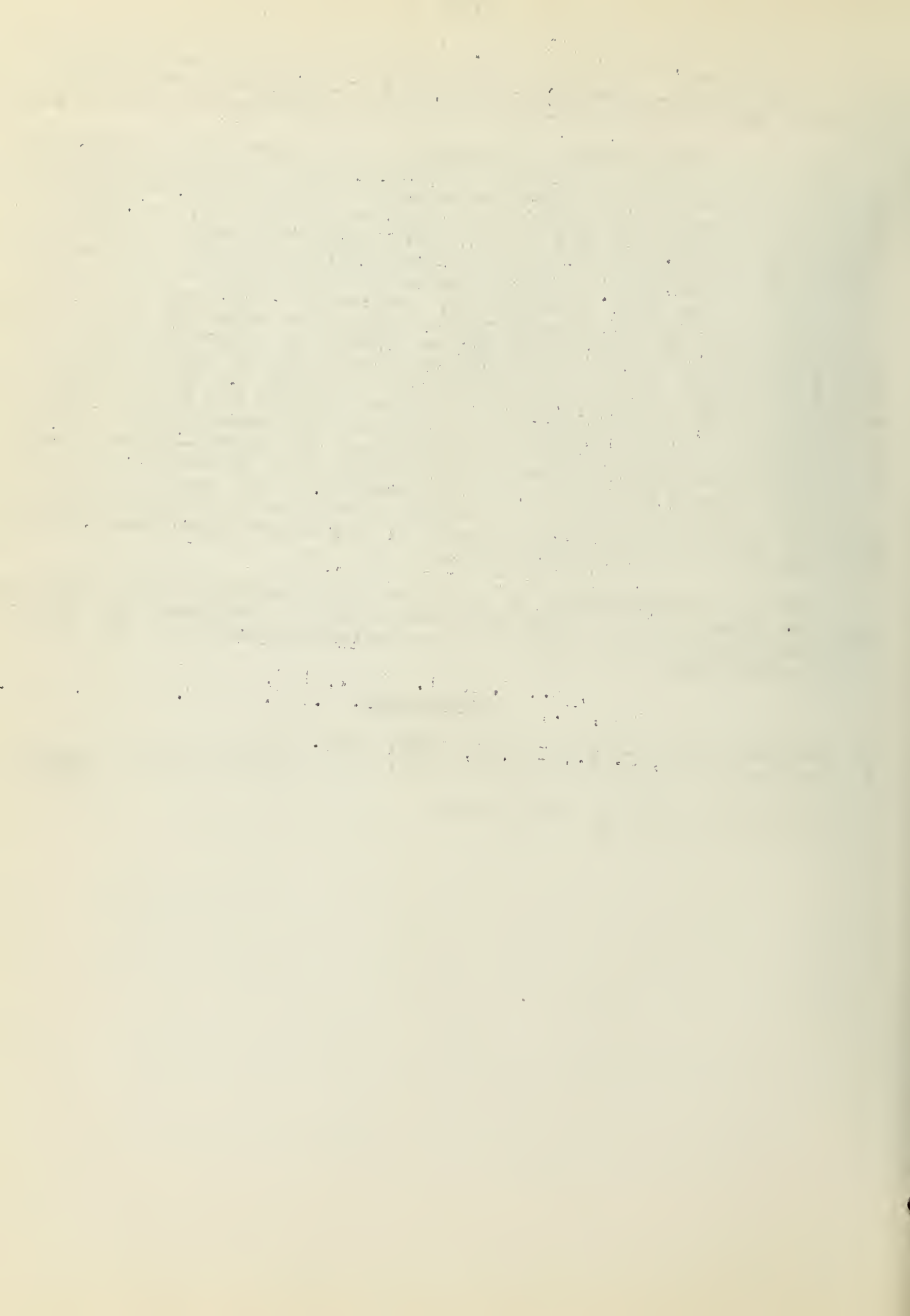
could be observed if solutions were prepared in the darkroom and observed immediately. Characteristic absorption peaks were observed at 310, 325, 338 and 395 m μ . The last peak was found to obey Beer's Law.

Thallium (III) oxinate, $Tl(C_9H_6NO)_3$, was prepared by essentially the same precipitation procedure as that used for the gallium compound except precipitation and digestion were carried out at room temperature. The first permanent precipitate appeared at a pH of 3.0, and precipitation was complete at pH 3.7-3.8. This compound appears suitable as a means of determining thallium gravimetrically, as shown by seventeen determinations on known solutions containing from 1.0 to 200.0 mg. of thallium. In the range 300-1000 m μ , three absorption peaks were observed at 328, 338 and 400-402 m μ for chloroform solutions of thallium (III) oxinate. The 400-402 m μ peak was found to adhere closely to Beer's Law in the concentration range 0.2-0.8 mg. of thallium (as the metal) per liter of solvent. Chloroform solutions of this compound are much less stable in sunlight than those of gallium and indium. Solutions prepared in the darkroom and protected from sunlight may be used for colorimetric determination of thallium. In acetate-buffered solutions, thallium (III) did not precipitate until a pH of 7.0 was reached while in sulfuric acid solutions it precipitated at about a pH of 1.0. In acetate buffered solutions, maximum extraction of thallium (III) by means of oxine in chloroform occurred in the narrow pH interval 6.5-7.0. The extraction was not quantitative.

The absorption spectra of solutions of quinoline, oxine, dichloroxine and dibromoxine in chloroform were observed and compared. The absorption peaks of the IIIB family oxinates were compared and relationships established.

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Glendall L. King

May 24, 1949

SOME PHYSICO-CHEMICAL STUDIES OF GALLIUM AND THALLIUM COMPOUNDS

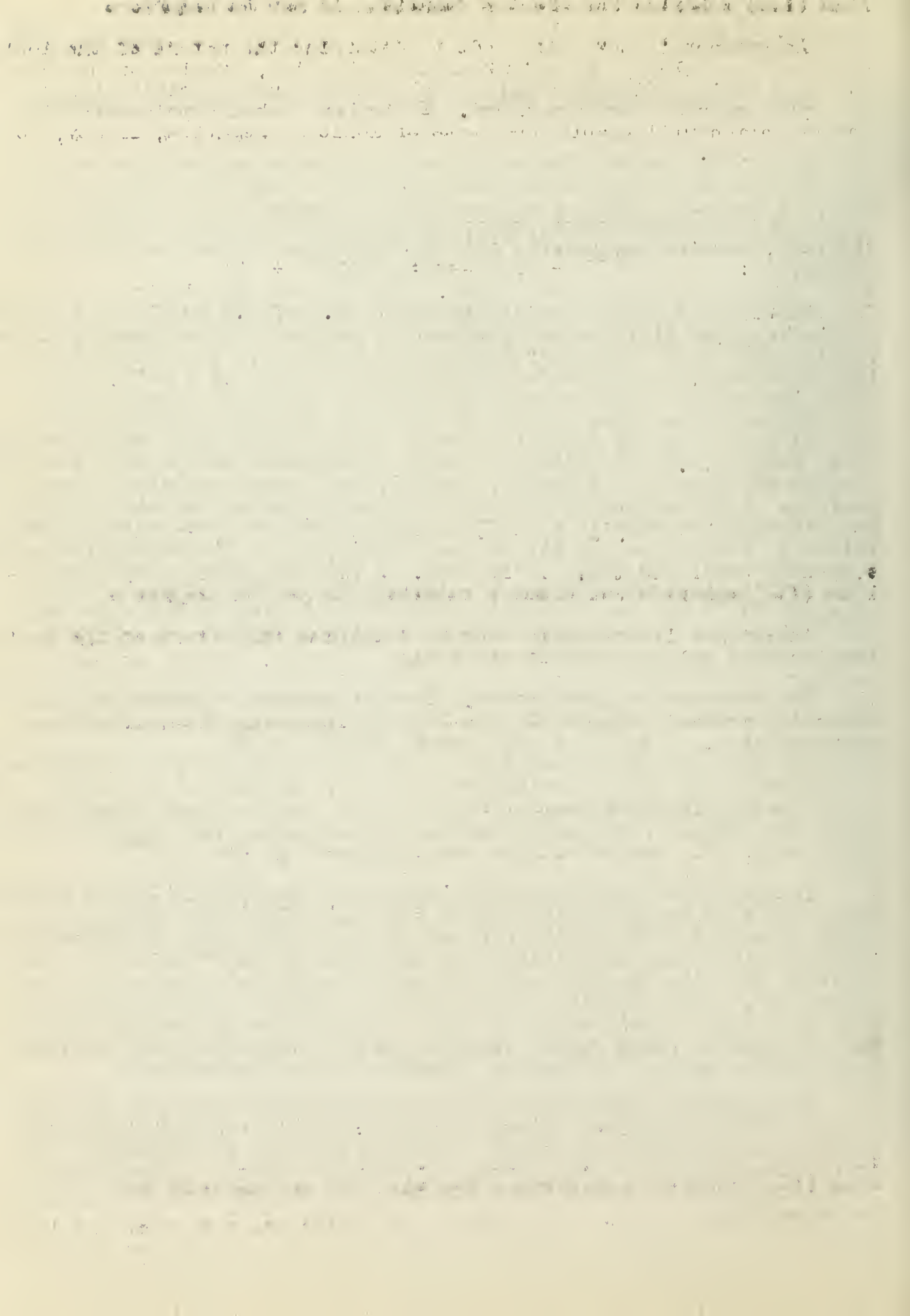
Among the characteristics of the gallium-indium-thallium family essential to their systematic study are trends and variations in basicity. A thorough study of the basicity of indium (III) compounds has previously been reported (1,2,3), and it was the purpose of this investigation to obtain comparable data for the gallium and thallium compounds.

Data were obtained for electrometric titrations with sodium hydroxide of gallium (III) sulfate, chloride, bromide, and nitrate solutions varying over wide concentration ranges. In the presence of sulfate ion, precipitation of hydrous gallium oxide begins at a mole ratio of added hydroxyl to gallium ion approximating 1.0 and is complete when this ratio reaches 3.0. In the presence of chloride, bromide, or nitrate ions apparent precipitation is delayed until this ratio reaches 3.0. Precipitation incidence is noted at somewhat higher and less reproducible pH values for chloride, bromide, and nitrate solutions than for sulfate. With sulfate solutions precipitation pH is but little effected by concentration changes at a given temperature but decreases as temperature is increased. In all cases, dissolution of the precipitate in excess hydroxyl ion occurs only when 5-6 moles of alkali have been added and the pH approximates 11. Solubility product values of the order of 10^{-35} and corresponding water solubilities of the order of 10^{-10} mole per liter indicate hydrous gallium oxide to be slightly less soluble than the indium compound.

The fundamental hydrolysis process in aqueous solution of gallium chloride, bromide and nitrate may be represented by the equilibrium expression: $Ga^{+++} + H_2O \rightleftharpoons GaOH^{++} + H^+$ water of hydration being neglected. The average hydrolysis constants for chloride and bromide solutions at 25 C°. of 3.5 and 3.9×10^{-4} respectively, indicate such solutions to be somewhat more highly hydrolyzed than those of the corresponding indium salt. For nitrate solutions at 25 C°, the hydrolysis constants average 3.0×10^{-4} .

Titration of thallium (III) sulfate solutions with sodium hydroxide show that the precipitation of thallium (III) oxide begins at a pH of about 1.0. Solubility product values of the order of 10^{-37} and corresponding water solubilities of the order of 10^{-10} mole per liter indicate that the thallium and gallium compounds have about the same solubility. With thallium (III) chloride, however, precipitation does not begin until a mole ratio of added hydroxyl ion to thallic ion of 0.6 and a pH of about 3.4 is reached. A more complete study of thallium (III) chloride and bromide solutions is now in progress.

An attempt is now being made to determine the nature of the ionic species in a solution of either gallium chloride, bromide or nitrate to which an insufficient amount of alkali to cause precipitation of the hydrous oxide has been added. It is hoped that a polarographic investigation will enable the state of ionic aggregation, if any, to be determined.



Glendall L. King

May 24, 1949

Preliminary experiments on the high temperature behavior of gallium oxide with the oxides of more basic metals have been undertaken. The progress of the sintering reactions is being followed by means of x-ray diffraction studies, and an attempt is being made to obtain a series of spinel-like compounds. Data so obtained may be of use in the evaluation of the basicity of gallium.

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